Factors Influencing Arsenic Release into Canterbury Groundwaters

A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Water Resource Management

at the University of Canterbury

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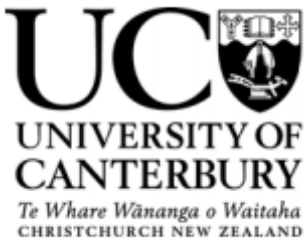

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Abstract

Arsenic is a toxic metalloid element which is naturally occurring in sediments, rocks, water and air. In some areas of the world, particularly Bangladesh, India, Pakistan, and Eastern Europe, elevated arsenic in groundwater causes health issues such as skin lesions, gastrointestinal disease, and cancer. Arsenic has been previously detected at concentrations exceeding the drinking water limit, 10 µg/L, in some groundwater wells in Canterbury. An investigation into the mechanism of arsenic enrichment in groundwater was undertaken. Four possible mechanisms of arsenic release were investigated: the reductive dissolution of iron and magnesium species with adsorbed arsenic, competitive sorption with phosphate, pH-related release in arid conditions, and oxidation of arsenic-bearing sulfide minerals. The microbial transformation of arsenic to more mobile species was not investigated in detail as no microbial studies were undertaken.

Initially an assessment of the existing groundwater monitoring data held by Environment Canterbury was carried out. In addition to this, nine wells with previously detected arsenic were selected and paired with nearby wells of a similar depth and with similar characteristics but lower historical arsenic. Samples were collected twice from each well in 2015; once in March or April (autumn), and once in July (winter). Each well was tested for conductivity, pH, temperature, and dissolved oxygen concentration and a full suite of chemicals including arsenic, manganese, iron, nitrate, phosphate, sulfate, cadmium, chromium, antimony and lead.

Significant positive correlations were observed between arsenic and iron, manganese, and dissolved reactive phosphorus (DRP) in both the analysis of Environment Canterbury data and the analysis of sampling results. Mutually exclusive relationships were observed between arsenic, sulfate and dissolved oxygen. Elevated arsenic concentrations were found in lower-lying wells with a flood risk, less permeable sediments, and silt-sized soil particles. The Environment Canterbury data showed that wells within 4.0 km of the coast had significantly elevated arsenic concentrations relative to those further inland, but this was not confirmed by the sampling analysis. The Environment Canterbury data also showed that

arsenic concentration was significantly higher in winter and autumn than summer and spring.

Due to the relationship between arsenic and chemicals that exist in, or are elevated in, reducing redox waters (i.e. anoxic); and the absence of arsenic in fully oxygenated groundwaters, it is suggested that elevated arsenic occurs to a greater extent in reducing conditions. A positive relationship between arsenic and organic carbon suggests that reducing conditions are contributed to by carbon-rich horizons in alluvial rock hosting the aquifer. This mechanism has previously been proposed for other arsenic-rich groundwaters in Marlborough and in other deltaic sediment hosted groundwater systems.

The findings show that elevated arsenic concentrations occur in wells with reducing conditions. Given this, and the significant relationships discussed previously, it is suggested that the reductive dissolution of iron oxide and manganese oxide minerals is the dominant mechanism of arsenic release into Canterbury groundwater.

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Abbreviations

CEC	Cation Exchange Capacity
CRM	Certified Reference Material
DL	Detection Limit
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DRP	Dissolved Reactive Phosphorus
GIS	Geographical Information Systems
HPIC	High Performance Ion Chromatography
HS	Hydrogen Sulfide
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
L	Litre
mg/L	Milligrams per Litre
µg/L	Micrograms per Litre
µS/cm	Micro Siemens per Litre
µm	Micrometres
OC	Organic Carbon
PT	Purge Time
T	Time
TC	Total Carbon
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
V	Volume

Chapter 1: Introduction

1.1 Introduction

Arsenic (As) contamination of drinking water is a global issue. In many different regions of the world As is present in drinking water at concentrations exceeding drinking water standards. Consumption of As in drinking water can lead to significant health issues in affected communities. Elevated As concentrations, exceeding the drinking water maximum allowable value (MAV) of 10 µg/L, have been measured in Canterbury groundwater. This thesis describes the results of an investigation into the mechanism of As release into Canterbury groundwater.

1.2 Groundwater

Groundwater is water present in the pores of soils and sediments, sitting on an impermeable layer so it cannot sink any further. When it rains, a portion of the rainwater seeps through the soils, sediments, and cracks in the rocks until it reaches the water table and becomes part of an aquifer (Bloetscher, 2014). Aquifers are classified as confined and unconfined, although 'semi-confined' aquifers also exist (Chong-Xi et al., 2006). Confined aquifers are contained within impermeable rocks and sediments (Chong-Xi et al., 2006). Unconfined aquifers have an impermeable bottom layer but water can move in other directions and can enter from the ground surface. Groundwater flows downstream incredibly slowly, over years, decades and centuries. It is accessed via wells which are drilled into the ground deep enough to penetrate the water table. Some wells require a pump to bring water to the surface but others are artesian with free-flowing water because of pressure from the confining layer (Bloetscher, 2014).

Groundwater is an important source of drinking water. It can become polluted and unusable because of leaching of contaminants from the surrounding land such as from landfills or

septic tanks (Bloetscher, 2014). Groundwater may also become polluted as a result of aquifer depletion because contaminants or trace elements can become more concentrated. Solute concentrations have also been shown to increase when water is drawn down rapidly by pumping (Ayotte et al., 2011). Some natural groundwaters cannot, or should not, be used because of their natural composition. For instance, there is concern over geothermal groundwaters in Waikato that are not used for drinking, but are still used for bathing and cooking (Lord et al., 2012).

1.3 Groundwater in the Canterbury Context

Groundwater is important in Canterbury as it is the source of the public water supply in Christchurch and in most of the surrounding area. Rainfall and snow melt are the two main mechanisms of aquifer recharge and the main source of surface water in Canterbury. Aquifer recharge is the term used to describe infiltration of water from the surface into groundwater. With low rainfall and high allocation of surface water, groundwater is becoming more important as a source of water for drinking, stock water, and irrigation. Several areas of Canterbury already have groundwater allocations that exceed the initial estimates of maximum groundwater allocation (Figure 1.1) (White & Scott, n.d.). It is important to guard the quality of the groundwater to maintain human health and the agricultural economy.

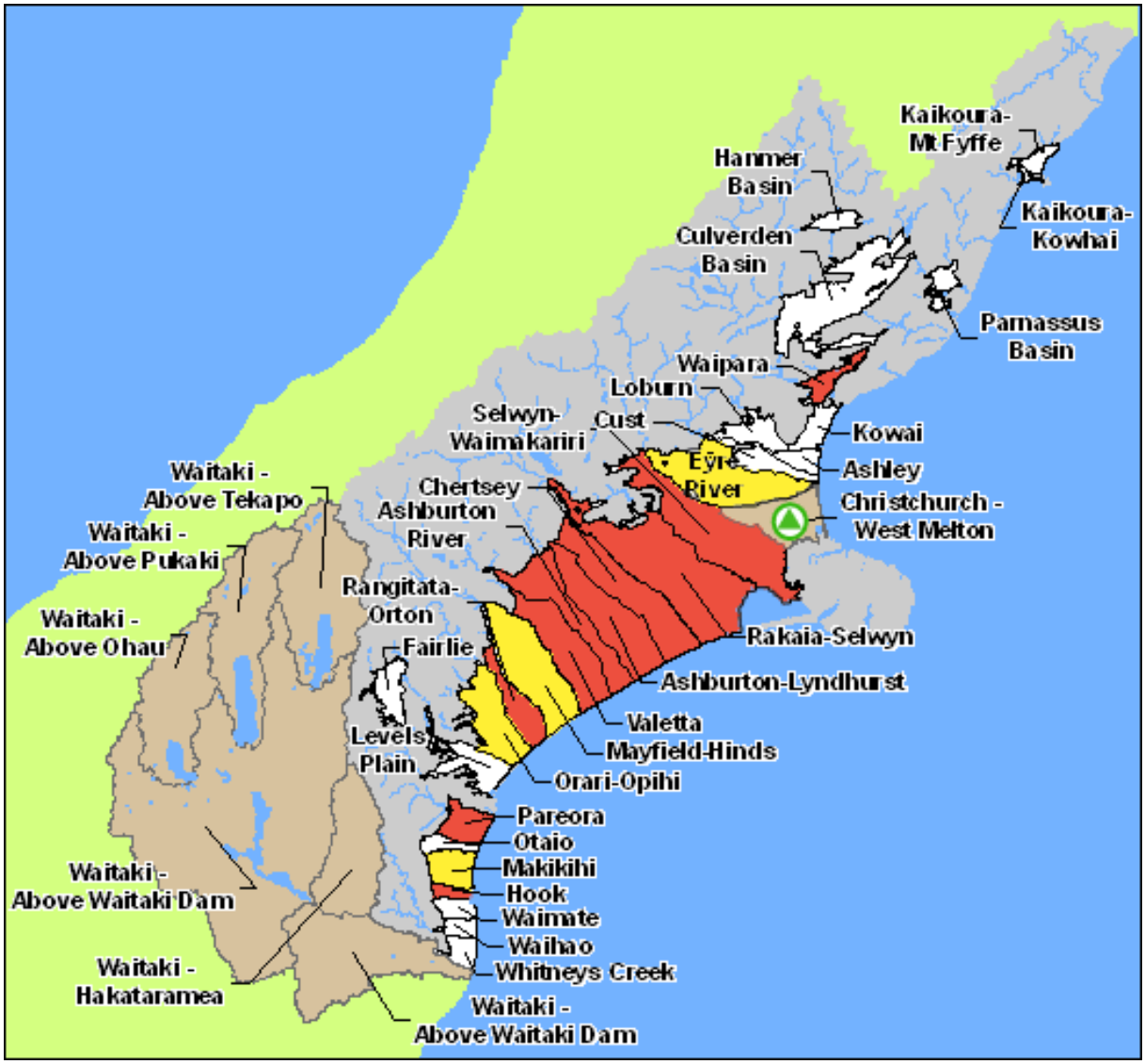


Figure 1.1: Map showing groundwater allocation in Canterbury (White & Scott, n.d.). Catchments shown in red exceed the initial estimate of maximum groundwater allocation, and catchments shown in yellow are near the initial estimate of maximum groundwater allocation.

1.4 Arsenic

1.4.1 Arsenic Chemistry and Groundwater

Arsenic (As) is a metalloid element that is present in trace amounts in soil, water, air, and rock (Gomez-Caminero, 2001). It has four possible oxidation states: -3, 0, +3, and +5 (Gomez-Caminero, 2001). Arsenic metal, As(0), is not soluble in water whereas As(III) and As(V), the +3 and +5 oxidation states, are both water soluble to a certain extent (Gomez-Caminero, 2001). As(III) is known as arsenite, has the chemical formula AsO_3^{3-}, and is the dominant species in reducing or anoxic environments (Gomez-Caminero, 2001). As(V) is

known as arsenate, has the chemical formula $ASO4^{3-}$, and is dominant in oxygenated environments (Gomez-Caminero, 2001). Methylated As compounds and arsenosugars occur naturally in marine environments (Gomez-Caminero, 2001).

Arsenic undergoes processes in groundwater that involve partitioning between the aqueous phase and solid phase. Iron (Fe), manganese (Mn) and aluminium (Al) oxides are an important sink for As in groundwater because they are common in the sediments and contain hydroxide groups that As can adsorb to (Stollenwerk, 2003). Other important processes include precipitation and dissolution of minerals, adsorption and desorption of arsenic species to and from sediments and suspended particulates, oxidation and reduction, and biological transformation (Stollenwerk, 2003). In aerobic conditions, As(III) in groundwater will oxidise to As(V) although this process is generally slow (Stollenwerk, 2003). The rate of this reaction can be increased by the presence of redox-sensitive species and light (Stollenwerk, 2003). Some microorganisms are capable of oxidising As(III) to As(V) (Stollenwerk, 2003). As(V) can be reduced to As(III) by hydrogen sulfide (HS) or hydrogen gas (H_2) (Stollenwerk, 2003). The speciation of As in groundwater varies depending on a variety of parameters including pH, redox potential and dissolved oxygen concentration. The toxicity of As compounds and methods of remediation depend on speciation (Jiang et al., 2013). In environments where As(III) is the dominant form of As, oxidation is required before remediation can be carried out, because As(V) can be removed more easily from groundwater than As(III) (Jiang et al., 2013).

1.4.2 Sources of Arsenic

Natural

The average concentration of As in New Zealand soils is 6-7 mg/kg (Environmental Risk Management Authority, 2003). Soils in Auckland, Tasman and Waikato contain As at quantities ranging from <2 to 58 mg/kg which in some cases exceeds the human health limit of 30 mg/kg (Gaw et al., 2006). Some of these soils contain significantly elevated As compared to the average of 6-7 mg/kg, which was predominantly due to anthropogenic effects rather than naturally elevated As (Gaw et al., 2006).

Anthropogenic

Vineyard posts treated with CCA (copper, chrome and arsenic) have been shown to leach As into the soil (Robinson et al., 2006). A study of CCA leaching in the U.S.A. found that acidic conditions and slow rainfall increased the amount of As leaching (Belluck et al., 2003). Concentrations of up to 0.2-5 ppm As have been measured in water from the surface of CCA-treated wood, resulting in raised As concentrations (3-350 ppm) in soils near treated wood compared to lower control levels (1.3-8.3 ppm) (Belluck et al., 2003).

Arsenic was used in pesticides before its toxic effects and persistence became known and residual As has been shown in the soil where cropping and orchards have previously occurred (Belluck et al., 2003). In Washington, U.S.A, land was treated with As-containing pesticides and there is residual As in the soils at concentrations up to 550 ppm (Belluck et al., 2003). Arsenic-based pesticides have been used historically in New Zealand but only one herbicide is still used, methylarsinic acid (Gaw et al., 2006). The study by Gaw et al. (2006) investigated trace element and DDT concentrations in horticultural soils in the North Island of New Zealand. Soil As concentrations ranged from <2 to 58 mg/kg As and orchard soil samples had higher As concentrations than other horticultural land uses due to the use of lead arsenate (Gaw et al., 2006). A study of historical sheep dip sites in the Tasman area showed that approximately half of these sites had soil As levels above the recommended maximum value (Murdoch, 2012). Arsenic can be concentrated in human waste – i.e. Sewage sludge, compost and animal waste including dairy manure, pig manure, and poultry manure (Belluck et al., 2003).

1.4.3 Arsenic in New Zealand Groundwaters

In 1999, As concentrations over 0.001 mg/L were detected in 55% of groundwater samples gathered from 121 wells in Canterbury (Ministry of Health, 2002). The highest concentration measured was 0.17 mg/L which was 17 times the maximum allowable value for drinking water in New Zealand (Ministry of Health, 2002). An arsenic concentration of 0.009 mg/L was measured in a well near Blenheim in 2001 (Ministry of Health, 2002). An arsenic concentration of 0.001 mg/L was measured in the far north of the North Island, 0.002 mg/L was measured at Ohiwa in the Bay of Plenty, 0.002 mg/L near Hastings and also near Napier,

0.004 mg/L was measured in a well near Gisborne, 0.002 mg/L near Whakatane, and 0.001 mg/L near Auckland (Ministry of Health, 2002). The average concentration of As in Hamilton drinking water is 0.0023 mg/L and the Waikato River contains approximately 0.025 mg/L As which is significantly over the drinking water standard (Environment Waikato, 2006). Approximately 10% of groundwater samples in Waikato exceed the drinking water standard (Environment Canterbury, 2006). One township in the Manawatu-Wanganui region had 30 wells which exceeded the 0.01 mg/L drinking water limit (Environment Waikato, 2006). Groundwater samples from the Taupo area reached up to 0.078 mg/L As while samples from the Coromandel reached 0.023 mg/L As, and samples from the Hamilton Basin reached 1.21 mg/L As (Environment Waikato, 2006). In the South Island, an As concentration of 0.003 mg/L was measured at Lyttelton (Ministry of Health, 2002). Groundwater with As severely exceeding the drinking water standard has been tested in Woodend (Ministry of Health, 2002).

1.4.4 Arsenic in Drinking Water as a Global Issue

Arsenic is a Global Issue

The presence of As in groundwater is a global issue and one which has had serious health implications for areas such as West Bengal, Pakistan, and Bangladesh. For example, approximately 35 million people are at risk of drinking water that is contaminated with As at unsafe levels in Bangladesh (Smith et al., 2000). The main mechanism of As release into groundwater in this area is the reductive dissolution of Fe and Mn oxides (Anawar et al., 2011). Bangladesh is one of the countries that have had severe As problems with their groundwater (Smedley, 2003). The most affected aquifers are associated with the Ganges-Brahmaputra-Meghna river system which covers a significant area in Bangladesh (Smedley, 2003).

There is a wide range of As concentrations in groundwater across Europe, with Turkey being the worst-affected country (Table 1.1) (Katsoyiannis et al., 2014). Several other countries including the Czech Republic, Finland, Italy, and Hungary also have significantly elevated As concentrations in some wells (Katsoyiannis et al., 2014). In some of these countries, the

elevated As is due to leaching from As-rich minerals, whereas in others, such as those in the Pannonian Basin in East-Central Europe, elevated-As is due to reductive dissolution of minerals which are not necessarily As-rich (Katsoyiannis et al., 2014).

Table 1.1: Maximum measured arsenic concentration in groundwater in European countries (Katsoyiannis et al., 2014).

Country/region	Concentration (µg/L)
Denmark	30
France	40
Belgium/Antwerp and Limberg	50
Germany/North Bavaria and Wiesbaden	150
Serbia/Vojvodina	150
Romania/Transylvania and Western Plain	200
Sweden	300
Iceland	310
Switzerland/Ticino, Wallis	370
Croatia	610
Spain/Duero Basin, Ambles Valley in Avila, Caldes de Malavella	615
Hungary	800
Finland	1,040
Italy/Volcanic areas of Ischia, Vesuvius, Etna, Stromboli	1,558
Czech Republic/Mokrsko	1,690
Turkey/Kutahya Plain	10,700

In the Pannonian Basin, Hungary and Romania have elevated concentrations of As present (Katsoyiannis et al., 2014). Arsenic in groundwater poses a health hazard to 600,000 people in the basin (Katsoyiannis et al., 2014). Arsenic concentration in groundwater varies globally (Table 1.1) In Croatia, groundwater As is elevated from the overlaying volcanic soils and approximately 200,000 people drink groundwater which has an As concentration ranging from 10-610 µg/L (Habuda-Stanic et al., 2006). However, no symptoms of arsenic poisoning have been reported in Croatia at the time of the study by Bošnjak et al. (2012). In Northern Greece, there is a limited water supply and some regions have groundwater As concentrations of up to 2,000 µg/L (Katsoyiannis et al., 2014).

Countries located in Central Europe and South America have significant As-related problems. In the Robles and La Banda counties of Santiago del Estero province in Argentina symptoms of chronic As contamination in water began appearing in 1983 (Bundschuh et al., 2004). The distribution of the As in shallow groundwater is patchy but in some places the concentration exceeded 400 µg/L which is eight times the legal limit of 50 µg/L in Argentina (Bundschuh et al., 2004).

Natural Sources

The typical concentration of As in groundwater is 1-2 µg/L but it is much higher in areas with volcanic rocks and soils which contain high quantities of sulfide minerals (Habuda-Stanic et al., 2006). The source of arsenic in Greece is thought to be geothermal fluids and the correlation between arsenic concentration and potassium (K), Mn and Fe in hydrothermal conditions supports that conclusion (Katsoyiannis et al., 2014). However, some areas have elevated-As concentrations which are caused by the reductive dissolution of Fe-oxides with sorbed As in alluvial deposits (Katsoyiannis et al., 2014).

Mining/Anthropogenic

Oxidation of sulfide minerals from mining can release arsenic into groundwater. For example, mining operations in the Phibun District of Thailand resulted in waste piles rich in arsenopyrite comprised of up to 30% As (Smedley, 2003). High As concentrations found in the shallow groundwaters of the area are thought to be caused by oxidation of the arsenopyrite and other sulfide minerals containing As from the mine (Smedley, 2003). In the Phibun District, As(V) is the predominant species of As, presumably because of the oxidising conditions (Smedley, 2003). Mining is not the only anthropogenic source of As. Pesticide use and timber treatment with CCA (copper, chromium and arsenic) can also be a source of As (Belluck et al., 2003).

1.4.5 Health Issues

Drinking water can be a significant source of arsenic exposure worldwide. The World Health Organisation (WHO) guideline maximum concentration of As in drinking water is now

10 µg/L, reduced from 50 µg/L in 1993 (Stollenwerk, 2003). Humans can be exposed to As through groundwater directly if they drink it, but there are also other routes of exposure, such as through food (Figure 1.2) (Jiang et al., 2013). A study by Immal Huq et al (2006) found that crops irrigated with As-laden water took up As to different extents depending on the type of crop and speciation of As. In particular, the vegetable 'arum' was found to take up as much as 150 mg/kg As (Immal Huq et al., 2006). In Bangladesh, citizens are exposed to As by consuming rice irrigated with As-rich water (Islam, 2008). These indirect routes of exposure could potentially cause As-related health effects in As-enriched areas.

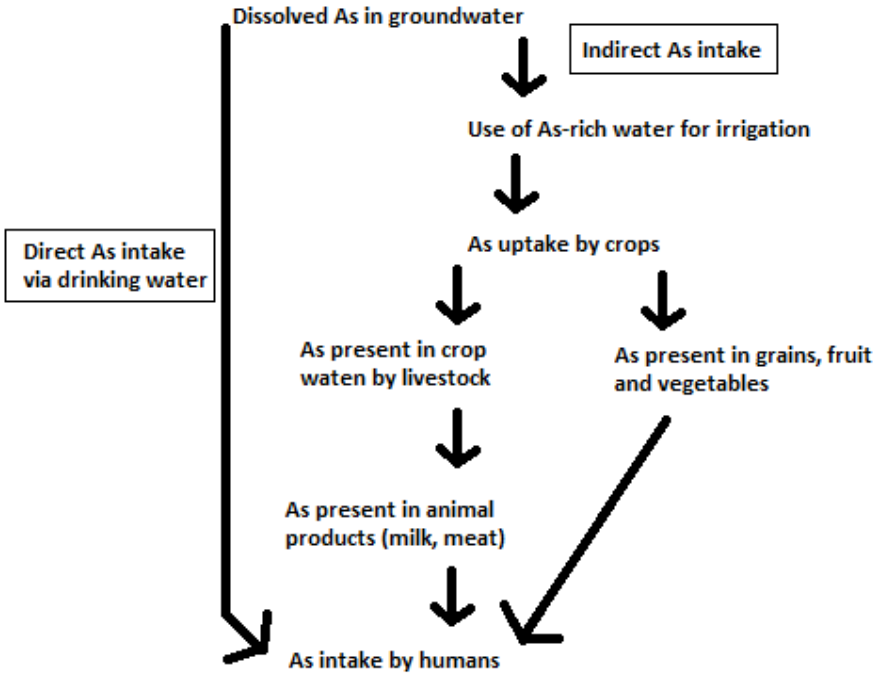


Figure 1.2: Route of human exposure to arsenic through food (Jiang et al., 2013).

Arsenic has several mechanisms of toxicity. It is toxic when ingested, inhaled or absorbed through the skin. Acute arsenic poisoning can cause gastrointestinal symptoms, disturb the functioning of the cardiovascular system and nervous system (Gomez-Caminero, 2001). Exposure to high concentrations of As can be fatal (Gomez-Caminero, 2001). Chronic arsenic poisoning can increase the risk of cancer, cause skin lesions or disease, bone marrow depression, and a variety of other symptoms (Gomez-Caminero, 2001).

The mechanism of toxicity of As(III) is via interactions between As(III) and the sulfhydryl sidechains of enzymes and other proteins, which denatures them and stops them from functioning (Duker et al., 2005). As(III) damages cells indirectly by assisting in the formation of reactive oxygen species which cause oxidative damage (Duker et al., 2005). Oxidative stress caused by As(III) can inhibit the action of glutathione reductase, which is an enzyme that protects cells (Duker et al., 2005). This effectively increases the damage As(III) does to cells as it reduces the capacity of cells to defend themselves. As(V) is toxic as it can substitute into enzymatic reactions in the place of phosphate and interfere with, or stop, the enzymes' functioning (Scott et al., 1993). Arsenic can also act as a mutagen by inhibiting DNA repair mechanisms (Abernathy et al., 1999).

Arsenic has also been shown to act as a carcinogen. A study in Chile found that there is a link between drinking water concentrations of As 50 μg/L or higher and skin cancer, as well as four types of internal cancer (Abernathy et al., 1999). Health issues related to drinking As-contaminated drinking water have different names in different countries. In Taiwan it is black foot disease, in Argentina it is Bell Ville disease, and in Thailand it is Kai Dam disease (Pokhrel et al., 2005). In the Phibun District of Thailand, over 1,000 people have been diagnosed with As-related skin disorders (Smedley, 2003). In Taiwan, As contamination of groundwater used for drinking has been linked to skin cancer with a dose-effect relationship, and high doses of As have been linked to black foot disease (Smith et al., 2000). High As concentrations have been detected in both the Southwest and Northeast coastal regions of Taiwan with concentrations up to 10 to 20 times the WHO guideline of 10 µg/L (Smedley, 2003).

Elevated As concentrations in groundwater have been associated with anaemia, particularly in pregnant women. A study in Romania found that women who were exposed to low-moderate concentrations of As in their drinking water were 2-3 times more likely to have reported anaemia diagnoses (Surdu et al., 2015). This relationship was corroborated by a cross-sectional study in West Bengal which found a higher odds ratio of anaemia occurring in women exposed to >800 µg/L As compared to women exposed to <50 µg/L of As (Surdu et al., 2015). It was also corroborated by a study in Chile which found that women exposed

to 33-53 µg/L of As via their drinking water had higher rates of anaemia than women who were not exposed to arsenic (Surdu et al., 2015). In the Antofagasta region Chile, the deaths of approximately 5-10% people aged thirty or greater are attributed to internal cancers such as bladder cancer and lung cancer caused by exposure to As (Marshall et al., 2007). A group of Japanese children were exposed to As-contaminated milk and experienced a greater incidence of severe hearing loss, epilepsy and mental retardation than is normal (Pokhrel et al., 2005). Doses of 70 to 180 mg of As can be fatal (Pokhrel et al., 2005).

1.4.6 Mechanisms of Arsenic Release

There are several different mechanisms by which As can be released into groundwater.

Reductive Dissolution of Minerals

In aquifers that have high levels of organic matter, strongly reducing conditions can be created at pH values that are near to neutral because DO is used up as organic matter degrades, and metals are likely to exist at lower oxidation states (Smedley & Kinniburgh, 2002). Arsenic adsorbed to minerals can be mobilised into groundwater by the reductive dissolution of those minerals including Fe and Mn oxides (Smedley & Kinniburgh, 2002). The biogeochemical cycle of As adsorption and precipitation involves Fe minerals and organic matter (Figure 1.3).

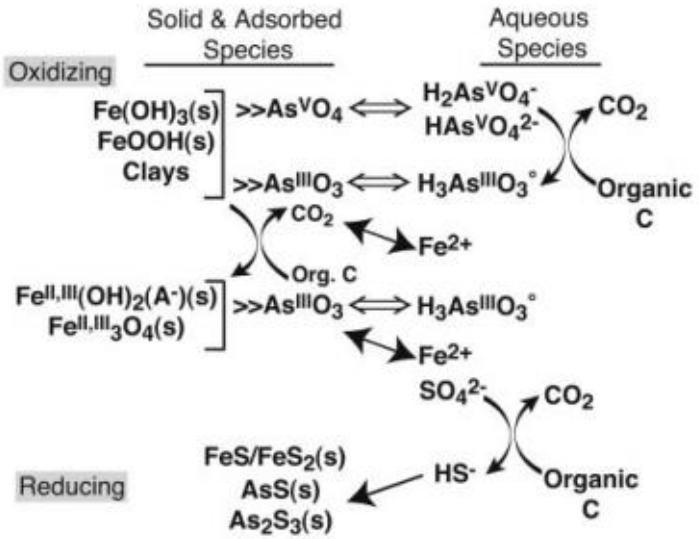


Figure 1.3: Biogeochemical cycle of arsenic adsorption onto iron minerals and its precipitation (O'Day et al., 2004).

This is perhaps the most widely studied and common mechanism of As release into groundwater. Bangladesh has relatively young and alluvial deltaic sediments and its groundwaters are strongly reducing with high concentrations of Fe, Mn, and dissolved organic carbon (DOC), phosphorus and hydrogen carbonate (Smedley, 2003). The primary source of As is thought to be Fe and Mn oxyhydroxides in sand and clay, while secondary sources include organic matter, and phyllosilicate minerals (Anawar et al., 2011). There was a strong correlation with an R^2 value of 0.85 between arsenic concentration and electrical conductivity in groundwater from shallow tubewells in Daudkandi, Bangladesh (Anawar et al., 2011). The mechanism of As release in Bangladesh is reductive dissolution. The sediments in West Bengal, India are Holocene alluvial and deltaic sediments with commonly occurring peat fragments which are similar to the type of sediments occurring in Bangladesh (Smedley, 2003). The groundwaters in West Bengal are strongly reducing with high concentrations of Fe, high alkalinity, and low concentrations of sulfate (SO_4) and nitrate (NO_3) (Smedley, 2003). The reductive dissolution mechanism of As-release into groundwater seems the most likely option in West Bengal as well as Bangladesh.

Reductive dissolution is also proposed as the controlling mechanism in elevated-As groundwaters in Hungary and Romania (Katsoyiannis et al., 2014). In Romania, the reducing conditions are indicated by negative Eh values of -50 to -200 mV (Katsoyiannis et al., 2014). An area of Serbia, in the southern Pannonian Basin, has elevated-As concentrations in conjunction with dissolved Fe, Mn, and ammonia, which indicates that the groundwater is highly reducing. This is also the case in Greece (Katsoyiannis et al., 2014). Therefore the reductive dissolution of Fe and Mn oxyhydroxides may be the controlling mechanism of As release to groundwater (Katsoyiannis et al., 2014).

Oxidation of Arsenic-Bearing Sulfides

The oxidation of As-bearing sulfides, including minerals such as arsenopyrite, has been proposed as another possible mechanism of As release into groundwater (see Equation 1.1) (Barringer & Reilly, 2013). This could be especially important in geothermal areas which have high levels of sulphur and corresponding high levels of As. New Zealand has significant

regions of geothermal activity, but these tend to be in the North Island more than the South Island.

Equation 1.1 $$FeAsS_{(s)} + \frac{11}{4}O_2 + \frac{3}{2}H_2O \rightarrow Fe^{2+}_{(aq)} + H_3AsO_{3(aq)} + SO^{2-}_{4(aq)}$$

The oxidation of arsenopyrite and other sulfide minerals is the mechanism of As-release in the shallow groundwaters of the Phibun District of Thailand (Smedley, 2003). In the Phibun District, As(V) is the predominant species of As, presumably because of the oxidising conditions (Smedley, 2003). Giménez-Forcada and Smedley (2014) reported that wells with elevated As concentrations in the Duero Basin of Spain were generally oxidising and alkaline with high nitrate concentrations. Nicolli et al (2012) found similar chemical relationships in the groundwaters of the Salí River Basin, Tucumán Province, Argentina. The proposed mechanism of release of As into groundwater for these studies was the oxidation of arsenic-bearing sulfide minerals (Giménez-Forcada & Smedley, 2014).

Microbial Transformation of Arsenic

Microorganisms such as bacteria, fungi and yeast are able to methylate inorganic arsenic compounds by replacing an OH group with a CH_3 group to form monomethylarsine (MMA) and dimethylarsine (DMA) (Bissen & Frimmel, 2003). Microorganisms can then convert these compounds to volatile As compounds (Bissen & Frimmel, 2003). In some conditions, microorganisms can mediate the release of As to groundwater or its adsorption onto mineral surfaces. For example, microorganisms can precipitate orpiment which is an As-bearing sulfide mineral (Equation 1.2) (Barringer & Reilly, 2013).

Equation 1.2 $$2HAsO_2 + 3HS^- + 3H^+ \rightarrow As_2S_3 + 4H_2O$$

In Mokrsko, Czech Republic the release of As in groundwater is mediated by Fe(III)-reducing bacteria which facilitate the release of As from Fe(III) hydroxides, Fe(III) oxides, and Fe(III) arsenates (Drahota et al., 2013). The microbial reduction of Fe(III) hydroxides requires the presence of organic carbon which is used for respiration (Islam, 2008). In Mokrsko, the microbial reduction of sulfate also triggers the formation of the mineral realgar which acts

as a sink for As (Drahota et al., 2013). In the Ganges River delta, it has been proposed that As is mobilised into groundwater by the reductive dissolution of Fe oxides and hydroxides (Islam, 2008). This reaction is facilitated by the use of organic matter by microorganisms for respiration (Islam, 2008). A study in Bangladesh found that in groundwaters that had low phosphate concentrations were nutrient-limiting in terms of microbe growth. As a result, the microbes solubilised hydroxyapatite which indirectly caused the release of As (Mailloux, et al., 2009).

Overall, microbial release of As is a similar process to the reductive dissolution of Fe- and Mn- oxides, but is facilitated by microorganisms and requires the presence of organic carbon. It was not investigated in the course of this research as no microbial studies were undertaken.

Competition for Mineral Sorption Sites

The amount of adsorption of As is determined by the properties of the mineral surface, pH, As speciation, and the concentrations of both As and other competing ions (Stollenwerk, 2003). The oxyanion species formed by phosphate, P(V), and arsenate, As(V), are similar chemically and have a similar affinity for surface sites (Stollenwerk, 2003). Increasing the concentration of P(V) in groundwaters has been shown to decrease the adsorption of As(V) to ferrihydrite at any pH and decrease the adsorption of As(III) at lower pH values (Stollenwerk, 2003). The competition for sorption sites may be the reason for a strong correlation observed between the concentration of phosphate and As in groundwater from shallow tubewells in a study by Anawar et al (2011). Other arsenate analogues can also interfere with adsorption of arsenate to mineral surfaces. These analogues include chemicals such as nitrate, which has similar chemical structures to arsenate (Environment Waikato, 2006)

pH-related Release from Sorption Sites

In arid and semi-arid areas, weathering and high rates of evaporation increase the pH of groundwater to over 8.5 (Smedley & Kinniburg, 2002). This alkaline pH causes the desorption of As from Fe mineral surfaces and its mobilisation into groundwater because

inorganic As species adsorb to minerals to a lesser extent when the pH is approximately 9 or above (Smedley & Kinniburgh, 2002).

Geothermal Conditions

Geothermal groundwaters may be naturally elevated in arsenic. This is particularly relevant in the Waikato region of New Zealand (Lord et al., 2012). In the Taupo area, geothermal wells have As concentrations several orders of magnitude higher than the drinking water standard. Some Greek groundwaters are rich in arsenic which is thought to have geothermal origins.

1.4.7 Arsenic in New Zealand Groundwater

There are existing issues with elevated As concentrations in groundwater in New Zealand. Geothermal wells near Lake Taupo have had As concentrations as high as 8900 μg/L which is 890 times greater than the recommended maximum value for safe drinking water (Bundschuh & Maity, 2015). In groundwater near gold mine sites in Otago, the As concentration is similar to the background concentrations of 10 μg/L in nearby surface waters (Craw et al., 2000). However, the As concentrations in groundwater where rocks contain arsenopyrite can reach 200 μg/L (Craw et al., 2000).

1.4.8 Arsenic in Canterbury

Veins containing arsenopyrite and gold deposits have been found in the Main Divide Fault Zone (Horton et al., 2001). In the upper Wilberforce valley of the Main Divide Fault Zone, located adjacent to Canterbury, there are mineral veins of quartz/ arsenopyrite/ pyrite/ chalcopyrite (Horton et al., 2001). The concentration of As in Wilberforce greywackes was found to be as high as 135 ppm while typical background concentrations from Torlesse sediments in other parts of the South Island are an average of 5.6 ppm As (Horton et al., 2001). The elevated As concentrations are considered to be due to fluid flows rather than any particular difference in the original composition of the greywackes (Horton et al., 2001).

Gouge samples from mineral veins collected from the Wilberforce valley (and to a certain extent, the Sealy Range) had a wide range of As concentrations, from normal background

levels to concentrations higher than 300 ppm (Horton et al., 2001). The average As concentration of 81.2 ppm compared to 1.7 ppm in other active fault zones in the South Island (Horton et al., 2001). In the veins and gouges where samples were collected, no As-bearing minerals were detected, nor were any sulfide minerals or Fe/Mn oxides, which suggests that the arsenic was adsorbed into calcite or quartz surfaces, or that it occurred within the calcite itself (Horton et al., 2001). There is a significance difference in As concentration in samples from the Main Divide Fault Zone compared to other areas in the South Island of New Zealand (Horton et al., 2001). The Main Divide Fault Zone has a much higher mean As concentration than any of the other regions (Figure 1.5).

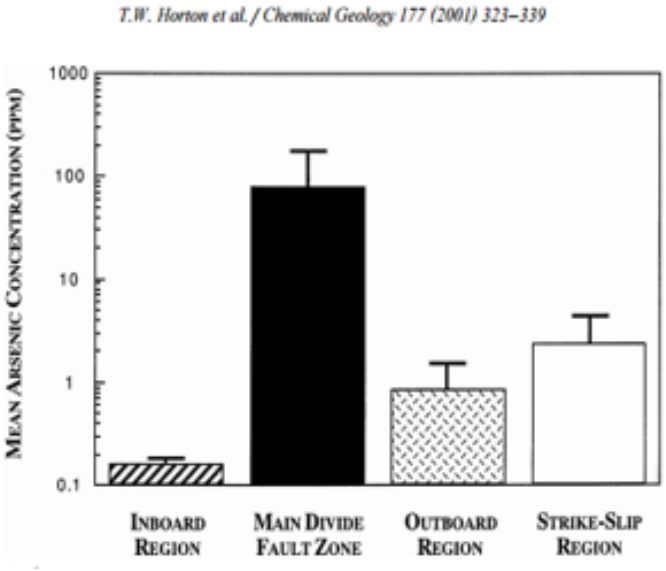


Figure 1.4: Mean arsenic concentration in calcite in gouge samples from mineral veins taken from different geological regions of the South Island of New Zealand. This figure was taken from Horton et al (2001).

A study in Canterbury showed high As concentrations in wells in coastal areas near Christchurch and in the Woodend-Waikuku-Saltwater Creek area which was likely due to nearby anthropogenic sources of As (Environment Waikato, 2006). High As concentrations have also been reported in soils beneath sheep dipping sites in Canterbury (Environment Canterbury, 2003). The concentration of As in soil varies depending on land use and can be contaminated by historical land uses (Gaw et al., 2006). The concentration of As in soil may correspond to the concentration of As in underlying groundwater, depending on the leaching potential of the soils and sediments.

1.4.9 Environmental Factors That Influence Arsenic Concentration

Relationships have been shown or between As concentration and season, depth and other factors which may cause spatial variation.

Seasonal Variation

There are contradictory reports for seasonal variation in As concentration in groundwater. A study in and around the Ganges River Basin in Nepal showed that the concentration of As in the groundwater varied both spatially and seasonally, being highest in summer and lowest in winter (Yadav et al., 2015). A study by Ayotte et al (2015) found that the concentration of As in groundwater in New England, and to a certain extent California, was significantly lower between January and June than it was between July and December. The researchers suggested this may be due to changes in groundwater level or pH. Another study in the U.S.A found that As concentration was not statistically different in summer compared to winter (Meinert, 2009). A third study in Alaska, U.S.A concurred with the study done by Meinert and showed no consistent seasonal variation in As concentrations in groundwater (Mueller et al., 1999). Yet another study in the U.S.A also showed that there is little, if any, seasonal variation in the concentration of As in groundwater (Thundiyil et al., 2007).

Spatial Variation

Arsenic concentration may vary spatially depending on environmental conditions and the concentration of other chemicals in the groundwater or soil. In China, a study found that wells with high As concentrations were clustered spatially in two strips along an alluvial lacustrine plain and suggested that this may be because these areas are conducive to rapid sediment deposition (Han et al., 2013). Meinert (2009) found that the concentration of As in groundwater varied spatially in the Lahontan Valley in Nevada.

Depth

No consistent relationship between As concentration and depth has been reported in the literature. Although the distribution of As in South and East Asia is highly variable, the highest concentrations are generally in shallower wells with a depth of 15 to 30 metres (Smedley, 2003). In contrast, a study in Burkina Faso showed that As concentrations were

higher in deeper wells (Smedley et al., 2007). The high-As aquifers of West Bengal, India were found to be between a depth of 10 metres and 80 metres with shallower and deeper groundwater being less affected (Smedley, 2003). However, the groundwaters of Taiwan showed less of a pattern with one area having As present in wells 100 to 280 metres deep and another area having As present in wells only 16 to 40 metres deep (Smedley, 2003).

1.5 Project Rationale

Concentrations of arsenic have previously been detected above the maximum allowable value (MAV) in Canterbury groundwater. Intake of As indirectly, by consumption of crops irrigated with elevated-As water, or animals which have consumed these crops, could be especially relevant in Canterbury in terms of both maintaining human health and for agriculture. Some sites have particular geological or geochemical features that make them more likely to contain As, as was previously discussed in the case of Bangladesh (Smedley, 2003). Studies have been carried out to investigate the concentration of As in minerals and bedrock in the Southern Alps which are inland from Canterbury (Horton et al., 2001). These studies found high As concentrations in particular veins and greywacke compared to other areas of New Zealand (Horton et al., 2001). This may translate to potential As-related problems in Canterbury.

Factors shown to be important in As-release in groundwater internationally include the presence of organic matter, As-bearing sulfide minerals, high concentrations of Fe and Mn, low DO concentrations and the presence of hydrothermal fluids and volcanic activity (Smedley, 2003) (Katsoyiannis et al., 2014) (Habuda-Stanic, 2006). It is important to know where As is coming from and how it mobilises in the groundwater to increase knowledge about groundwater resources in Canterbury and to prevent As contamination from becoming a problem.

1.5.1 Project Aim and Objectives

The aim of this thesis is to determine factors affecting the concentration of As in Canterbury groundwaters, and to use this to identify a possible mechanism of As release into Canterbury groundwaters.

There are several objectives to meet in order to achieve this:

- Analyse the groundwater monitoring data collected to date (by Environment Canterbury) in order to determine relationships between As and other variables including Fe, Mn, DO, organic matter and SO_4.
- Confirm these relationships by further sampling and analysis.
- Determine whether the concentration of As in groundwater has any spatial or temporal patterns, using a combination of data obtained from Environment Canterbury and further sampling.
- Use the information gathered to propose a mechanism of As release into Canterbury groundwater.

1.5.2 Thesis Structure

Chapter 2 outlines the analytical methods used to investigate Environment Canterbury data and the methods used to collect samples, test samples, and analyse statistical data. Chapter 3 presents the results of the statistical analysis of Environment Canterbury data and discusses the significance of the results, trends identified, and the interpretation of those trends. Chapter 4 presents the results from sampling and discusses the findings. It also compares the findings from sampling analysis back to the findings from Chapter 3. Chapter 5 states the conclusions reached in Chapters 3 and 4, discusses the limitations of the study and outlines further research that could be helpful in determining factors that influence the concentration of arsenic in Canterbury groundwater.

Chapter 2: Methodology

2.1 Introduction

Chapter 2 describes the methods used in this thesis. There are two components to this research:

1. Analysis of existing groundwater data from Environment Canterbury;
2. Sampling and analysis of paired wells.

2.2 GIS Mapping

Data obtained from Environment Canterbury's groundwater monitoring database, courtesy of Mr Carl Hanson, was used to create GIS maps showing the distribution of arsenic (As), iron (Fe), manganese (Mn), dissolved organic carbon (DOC), dissolved oxygen (DO), and sulfate (SO_4) in Canterbury's groundwater. When a particular analyte was not measured simultaneously with As, the value measured nearest to the time of the As test was used. ArcGIS Online and used to create a multi-layered map.

2.3 Analysis of Environment Canterbury Data

The values of each parameter at each well were plotted against the concentration of As to determine whether there was a linear correlation between the variables. The Pearson's correlation coefficient, r, for these graphs was determined, and *p*-values were calculated. These were used to determine whether there was a relationship between the variables and As concentration. Where a relationship other than a linear correlation was observed, t-tests were used to analyse the relationship. Where the concentration of a chemical was less than the detection limit, a value of half the detection limit was used.

A series of T-tests were conducted to determine whether there was a relationship between As concentration and distance from the coast. One side of a delineating line was defined as coastal and the other as inland. The arbitrary line began at 1km from the coast and slowly shifted inwards at intervals of 2 km, 2.5km, 3km, 3.5km, 4 km, 4.5 km, 5 km, 5.5 km, 6 km, 7 km, 8 km, 10 km, 15 km, 20 km, 25 km, 30 km, 40 km, 50 km, 60 km. Pearson's correlation coefficient was also used to determine the relationship between As concentration and distance from the coast. Paired t-tests were used to determine whether there was a statistically significant difference in As concentration between seasons. Information about soil characteristics found in GIS maps created by Landcare Research was used to create box and whisker plots. These plots showed how wells with different concentrations of As were distributed amongst areas with different soil and environmental characteristics.

A paired t-test was carried out using data obtained from the Environment Canterbury groundwater monitoring database to investigate whether there was any difference in groundwater chemistry caused by the Canterbury earthquakes. The wells selected were chosen because As had been tested prior to the earthquakes and also after the earthquakes. The t-test was used to determine whether the mean As concentrations in selected wells after the Canterbury earthquakes were significantly different to the mean As concentrations in in the years following the earthquakes.

2.4 Groundwater Study

2.4.1 Well Selection

Eighteen wells were selected for sampling from the Environment Canterbury groundwater monitoring database. Wells were assigned a code to maintain the anonymity of well owners. The numbering begins at 1 and to 9, where 1 is the northernmost well and 9 is the southernmost well. The wells were allocated to two groups; wells labelled 'A' are elevated-As wells and wells labelled 'C' are low As, or control, wells. The selection criteria for wells for each group are presented below.

Selection criteria for wells in group A:

- Previously been found to contain detectable levels of As.
- Located within Canterbury, preferably within two hours' drive of Christchurch.
- Has a working pump, or ability to use a portable surface pump.
- Permission granted by the owner to collect groundwater samples.

Selection criteria for wells in group C:

- No As previously detected.
- Near to, and with a similar depth to, a group A well.
- The environment surrounding the well is similar to that of the group A well to which it has been paired. For example, similar soil type, vegetation, and soil moisture.
- Located within Canterbury, preferably within two hours' drive of Christchurch.
- Either still in use, or with ability to use a portable surface pump.
- Permission granted by the owner to collect groundwater samples.

Unfortunately during the second round of sampling in July there was no access to well 6C because the well pump had been turned off. Instead, a sample was taken from a well of a similar depth that was no more than 8 metres from well 6C. This well will be referred to as well 6Cb.

The sediment type, vegetation type, and soil profiles at each site were identified using maps created by Landcare Research. The full characteristics of the well locations can be found in Appendix 2, however, a summary of the most relevant sections of this information is included in this chapter (Table 2.1).

Table 2.1: Summary table of key environmental characteristics of selected sampling wells (Environment Canterbury et al., 2013) (Landcare Research, 1996).

Well	Location	Rock Type	Land Use	Land Suitability	Ecosystem
1A	Kaikoura area	Loose sedimentary	Stock farming. Arable farming.	Suitable for multiple uses. Primarily for arable farming.	Agricultural. 10-20% indigenous cover. Exotic grasslands.
1C	Kaikoura area	Loose sedimentary	Stock farming.	Arable farming.	Agricultural. 10-20% indigenous cover. Exotic grasslands.
2A	Amberley area	Loose sedimentary	Stock farming.	Limited arable. Intensive grazing.	Agricultural. <10% indigenous cover. Exotic grasslands.
2C	Amberley area	Loose sedimentary	Stock farming. Residential.	Limited arable. Intensive grazing. Forestry.	Agricultural. <10% indigenous cover. Exotic grasslands.
3A	Waikuku area	Loose sedimentary	Stock farming.	Multiple land use, particularly arable.	Agricultural. <10% indigenous cover. Exotic grasslands. Swamp.
3C	Waikuku area	Loose sedimentary	Residential.	Forestry. Pastoral use.	Exotic forests. <10% indigenous cover. Marsh.
4A	Ohoka area	Loose sedimentary	Residential.	Multiple land use, particularly arable.	Agricultural. <10% indigenous cover. Exotic grasslands. Swamp.
4C	Ohoka area	Loose sedimentary	Stock and arable farming.	Multiple land use, particularly arable.	Agricultural. <10% indigenous cover. Exotic grasslands.
5A	Northwest Christchurch	Loose sedimentary	Residential. Some stock grazing.	Arable. Intensive horticulture.	Urban/agricultural. <10% indigenous cover. Crops and exotic grasslands.
5C	Northwest Christchurch	Loose sedimentary	Residential. Industrial.	Very limited arable.	Urban. <10% indigenous cover.
6A	Coastal Christchurch	Unknown	Residential. Recreational.	Unknown.	Urban. <10% indigenous cover. Exotic grasslands.
6C/ 6Cb	Northeast Christchurch	Unknown	Residential.	Unknown	Unknown.
7A	Coastal Christchurch	Unknown	Residential. Recreational.	Unknown.	Urban/coastal. <10% indigenous cover.
7C	Coastal Christchurch	Unknown	Residential. Recreational.	Unknown	Urban/coastal. <10% indigenous cover.
8A	Southeast Christchurch	Loose sedimentary	Residential. Industrial.	Arable. Intensive grazing.	Wetlands. 10-20% indigenous cover. Swamp.
8C	Southeast Christchurch	Loose sedimentary	Residential. Industrial. Some stock grazing.	Limited arable. Intensive grazing.	Wetlands. 10-20% indigenous cover. Swamp.
9A	Southeast Christchurch	Loose sedimentary	Industrial.	Limited arable. Intensive grazing.	Urban, 10-20% indigenous cover. Swamp.
9C	Southeast Christchurch	Unknown	Residential.	Unknown	Urban, 10-20% indigenous cover. Exotic grasslands. Swamp.

2.4.2 Well Sampling Procedure

Groundwater sampling was carried out twice: Once in March/April and once in July. During sampling I was accompanied to approximately half of the wells by David Evans, a Senior Groundwater Officer from Environment Canterbury. Wells were purged prior to sampling. The purge volume was three time the volume of the well (Equation 2.1), which is the volume Environment Canterbury purges during their groundwater monitoring (Hanson, 2012).

Equation 2.1 $$\mathrm{PV}\ (m^3) = 3[2(\mathrm{WD} - \mathrm{WL})\pi(\frac{\mathrm{WCD}}{2})^2]$$

WD = Well depth (m)

WL = Water level (m)

WCD = Well casing diameter (m)

To determine the purge time, PT, at each well, Equation 2.2 was used.

Equation 2.2 $$\mathrm{PT\ (seconds)} = \left(\frac{PV}{10}\right)\mathrm{T}$$

T = Time for 10 L bucket to fill

After purging, samples were collected either directly from the sampling valve of the well or from piping attached to the well. The sampling apparatus consisted of a brass plumbing fitting with two taps attached as sampling points and a purge hose and flow cell attached to purge the well and collect data from field probes. The flow cell consisted of a short length of hose attached to a small plastic chamber. Water entered in the bottom of the chamber and flowed through the chamber, exiting through a hole in the top of the cell (Figure 2.1).

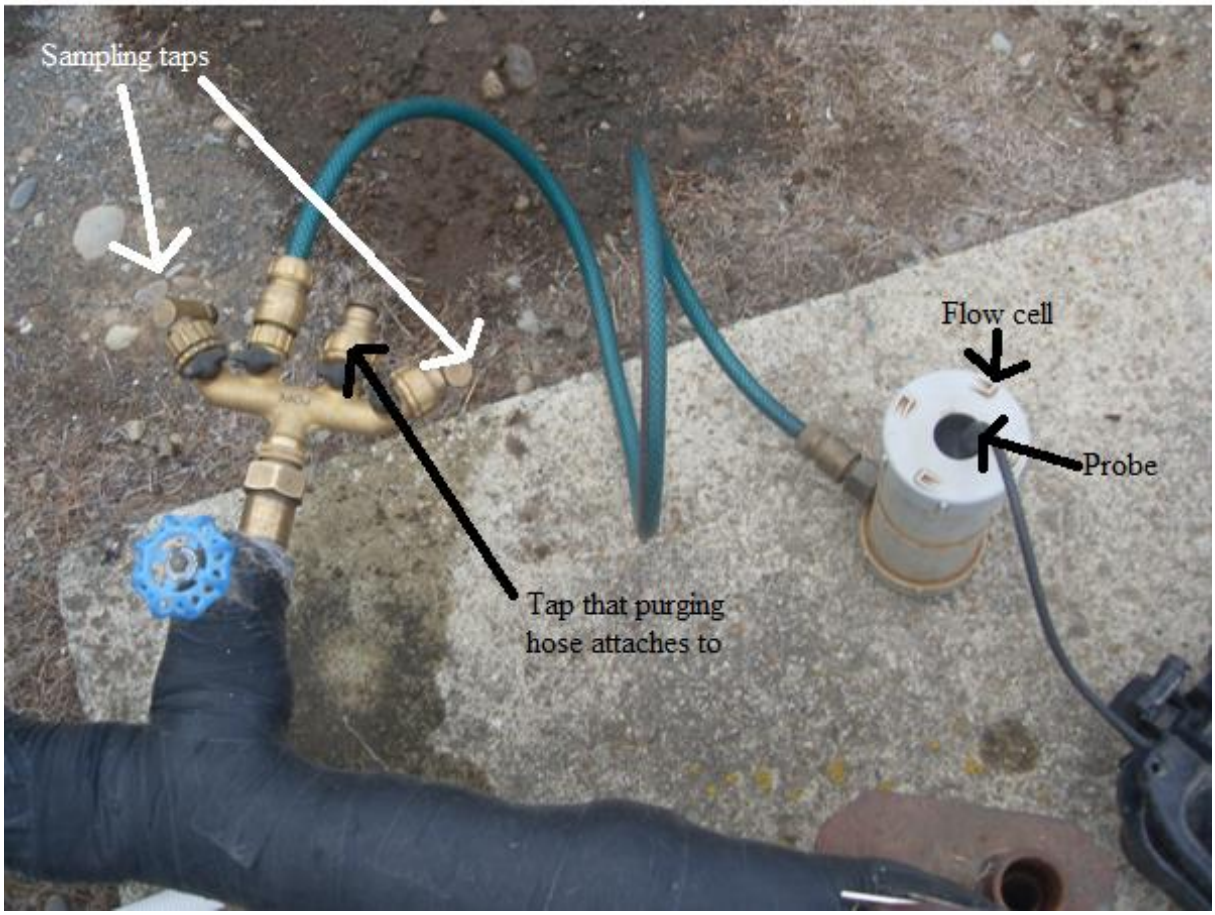


Figure 2.1: Configuration of well sampling apparatus.

The conductivity and pH probes were calibrated prior to each day of sampling using standard solutions. The dissolved oxygen (DO) probe was calibrated in the laboratory prior to use. The sampling taps were not used at all wells as not all wells had the appropriate plumbing for them to be attached. At wells where the sampling taps could not be connected, the access point nearest to the bore itself was used as the sampling point. The apparatus varied slightly between sites (Table 2.2). Approximately half of the wells had pumps installed, either surface or submersible. Two of the wells were artesian and did not require a pump in order to sample. A third well was artesian but not flowing in April so a pump was used. The remaining wells were sampled using the petrol-based surface pump provided by Environment Canterbury.

Table 2.2: Description of the apparatus used at each well.

Well	Sampling Apparatus Used		Flow Cell Used		Sample Taken Directly from Source	Pumped or Artesian?
	April	July	April	July		
1A	Yes	No	Yes	No	No	Artesian
1C	No	No	No	Yes	Yes	Pumped
2A	Yes	No	Yes	Yes	No	Pumped
2C	No	No	No	Yes	Yes	Pumped
3A	Yes	No	Yes	Yes	No	Artesian
3C	No	No	No	No	Yes	Pumped
4A	Yes	No	Yes	Yes	No	Pumped
4C	No	No	No	No	Yes	Pumped
5A	Yes	No	Yes	Yes	No	Pumped
5C	No	No	Yes	Yes	Yes	Pumped
6A	No	No	Yes	Yes	Yes	Pumped
6C/6Cb	No	No	Yes	Yes	Yes	Pumped
7A	No	Yes	Yes	Yes	Yes	Artesian
7C	Yes	Yes	Yes	Yes	No	Pumped
8A	Yes	Yes	Yes	Yes	No	Pumped
8C	Yes	Yes	Yes	Yes	No	Pumped
9A	No	No	Yes	Yes	Yes	Pumped
9C	Yes	No	Yes	Yes	No	Pumped

2.4.3 Groundwater Sample Collection and Storage

Total and filtered water samples were collected from each well. Filtered samples were filtered using a 0.45 µm Millex filter on-site. Environmental blanks were taken at some sites by exposing ultrapure Milli-Q water in a 50 mL centrifuge tube to air at the site for two minutes. During the first round of sampling an environmental blank was taken at well 6A. During the second round of sampling, one blank was taken per day of sampling, at wells 1A, 3A, 5A, 7A, and 9A. A sample duplicate was also taken from each site during the second round of sampling.

Table 2.3: The methods used to collect samples for testing different parameters.

Sample	Container	Filtered? (0.45 µm)	Number collected at each site	Other notes
Dissolved As, trace elements, and cations	Brand new Thermo fisher LabServ 50 mL polypropylene centrifuge tube	Yes	2	One sample was acidified, one sample was not
Total As, trace elements, and cations	Brand new Thermo fisher LabServ 50 mL polypropylene centrifuge tube	No	2	One sample was acidified, one sample was not
Anions	Brand new Thermo fisher LabServ 50 mL polypropylene centrifuge tube	Yes	1	
TOC/TC/TIC	Amber glass jar	No	1	
NO_3	Brand new Thermo fisher LabServ 50 mL polypropylene centrifuge tube	Yes	2	
DRP	Brand new Thermo fisher LabServ 50 mL polypropylene centrifuge tube	Yes	2	

Samples were transported back to the laboratory using a 40 L chilly bin filled with no less than 3 kg of ice. The ice was replaced every 3-4 hours where necessary. Prior to storing the samples, samples to be analysed for cations, trace elements and As were acidified with 100 µL of concentrated ultrapure nitric acid. Samples were stored then in a chiller at Lincoln University at 2-4°Celsius.

2.5 Analysis

2.5.1 In situ Physicochemical Parameters

A HACH HQ40d portable multi meter was used to measure DO concentration with a HACH LDO101 probe, conductivity with a HACH CDC401 probe, pH with a HACH IntelliCAL pH PHC101 probe. Temperature was measured using the DO probe. The Hach portable meter was used in conjunction with the flow cell to measure in situ conditions. Exposure to air prior to DO measurements was minimised by using a pump and/or sampling apparatus

including the flow cell where possible (Figure 2.1). A Thermo scientific ORION AQUAfast AQ4500 turbidimeter was used to measure turbidity at each site during the second round of sampling in July.

2.5.2 Cations and Trace Elements

Arsenic and other trace elements and cations including sodium (Na), magnesium (Mg), aluminium (Al), potassium (K), calcium (Ca), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), antimony (Sb) and lead (Pb) were analysed using an Agilent 7500cx ICPMS. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measures combined As(III) and As(V) oxidation states. Samples were prepared for ICP-MS in four different ways. Two trace element and cation samples from each well were filtered and two were not. One filtered sample was acidified and one was not acidified, one unfiltered sample was acidified and one was not acidified. This was to enable acidified and unacidified samples to be compared because under certain circumstances hydrogen sulfide (HS) present in groundwater will react with the acid and As to create the mineral orpiment, which precipitates out of solution (Equation 2.3). If this happens, the measured concentration of As would be less than was actually present in the groundwater.

Equation 2.3 $$2AsO_4^{5-} + 5H_2S + 6H^+ \rightarrow As_2S_3 + S_2 + 8H_2O$$

The unacidified samples were also tested to determine whether there was a significant difference between acidified and unacidified samples that could be attributed to the formation of orpiment. Two other samples were unfiltered so the total As could be determined.

Samples of approximately 5-10 mL were prepared for ICP-MS analysis in the clean room at the chemistry department of the University of Canterbury. The standards used for each chemical submitted for ICP-MS analysis were 0.0 µg/L, 0.1 µg/L, 1.0 µg/L, 10 µg/L, 100 µg/L, 100 µg/L. Solutions of 20 parts per billion (ppb), 2.0 ppb and 0.0 ppb were also included at the beginning, end and middle of the ICP-MS analysis. The detection limits (DL) for As and

other trace elements (Table 2.4) were determined two ways and the highest of the detection limits was used. The first method involved dividing the standard deviation of a series of standard solutions by the slope of the calibration curve and multiplying the result by 3.3 (Equation 2.4) (International Consultant on Harmonisation Expert Witness Group, 1994).

Equation 2.4 $$DL = 3.3(\frac{standard\ deviation}{slope})$$

The detection limits for cations and trace elements, including arsenic, were checked by comparing them to the ICP-MS calibration results to determine which standard solution was within 15% of the known concentration. The higher of the two numbers was used as the detection limit.

Table 2.4: Detection limits for cations and trace elements including arsenic.

Analyte	Detection Limit	Analyte	Detection Limit
Fe	1.0	Sb	0.4
Al	1.0	Cu	1.0
As	0.1	Zn	10.0
Co	0.1	Pb	0.1
Ni	0.1	Cd	0.1
V	0.1	Mn	0.1
Cr	0.1	Na	10.0
Mg	10.0	K	15.3
Ca	10.0		

2.5.3 Major Ions

Anions

All samples for ion chromatography analysis were prepared in the SABRE laboratory in the Geology Department of the University of Canterbury and analysed using high performance ion chromatography (HPIC) by Mr Matthew Cockroft, a technician from the Geology Department of the University of Canterbury. The HPIC analysis was carried out using the

DIONEX ICS-2100 instrument. The column in this instrument was 4mm AS19 + AG19 Guard with an eluent of 10 $mMolL^{-1}$ K hydroxide (KOH). The eluent flow was rate was 1 mL/minute. The gradient method was used, in which two solvents are included, one weak (water) and one strong (KOH). The proportion of the weak solvent starts out high and gradually decreases as the stronger solvent correspondingly increases. The mixed anion standards used for HPIC analysis were 0.1 mg/L, 1.0 mg/L, 5.0 mg/L, 25.0 mg/L, 50.0 mg/L and 100.0 mg/L. The anions tested for were chloride (Cl), nitrate (NO_3) and sulfate (SO_4). For sites with high conductivities, both diluted and undiluted samples were tested. Samples 2A and 2C were diluted 1:2 and 8A was diluted 1:3. The detection limits (Table 2.5) were determined using the signal to noise ratio by Mr Matthew Cockroft.

Table 2.5: Detection limits for anions.

Anion	Detection Limit (mg/L)
SO_4	0.015
Cl	0.05
NO_3	0.05

2.5.4 Dissolved Reactive Phosphorous

Dissolved Reactive Phosphorus, DRP, was tested using a HACH DR890 spectrophotometer at Lincoln University. Calibration curves were created by diluting a 2 mg/L stock solution of DRP to create standard solutions of 0.2 mg/L, 0.3 mg/L, 0.4 mg/L, 0.6 mg/L, 0.8 mg/L, 0.9 mg/L, 1.2 mg/L DRP. The spectrophotometer was zeroed with deionised water. A combined blank reagent was made by mixing 25 mL of 5 mol/L H_2SO4 and 7.5 mL of 0.0324 mol/L ammonium molybdate. It was replaced at least once every four hours before it became unstable. A combined sample reagent was then made up from 25 mL of 5 mol/L H_2SO4, 2.5 mL of 0.00844 mol/L antimony K tartrate, 15 mL of 0.100 mol/L ascorbic acid and 7.5 mL of ammonium molybdate. The combined sampling blank excluded the chemicals which would cause the reagent to react with DRP present in groundwater to form a coloured compound.

For the calibration, 1.6 mL of the combined sample reagent was added to each of the 10 mL standard solutions at 1 minute intervals. After ten minutes, the absorbance of each solution

was determined at a wavelength of 880nm at 1 minute intervals after initially zeroing the spectrophotometer. Calibration curve 1 (Figure 2.2) was used to determine the DRP concentration for the samples from all sites except 1A and 1C. That is, all water samples with a concentration less than 0.8 mg/L were tested using the cuvette with a 5 cm pathlength and the sites with concentrations over 0.8 mg/L were tested using the cuvette with a 2 cm pathlength.

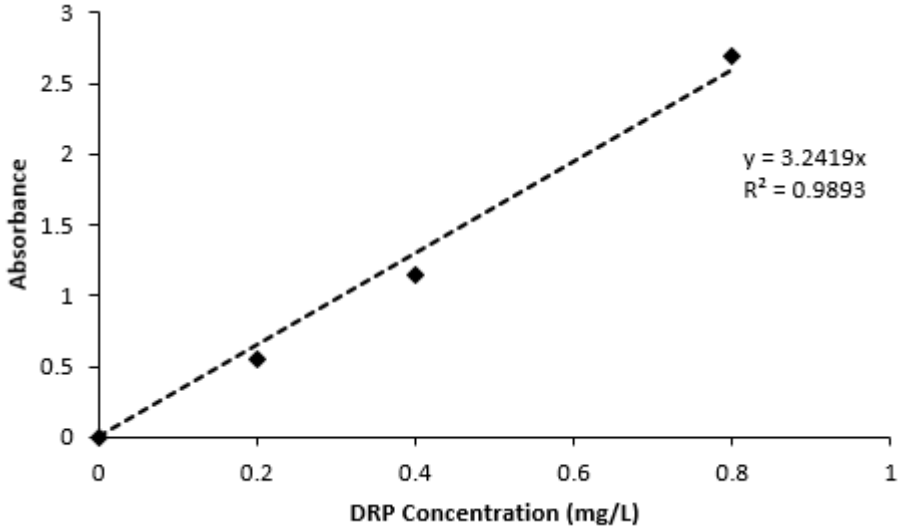


Figure 2.2: Calibration curve 1 for DRP for the cuvette with 5 cm path length.

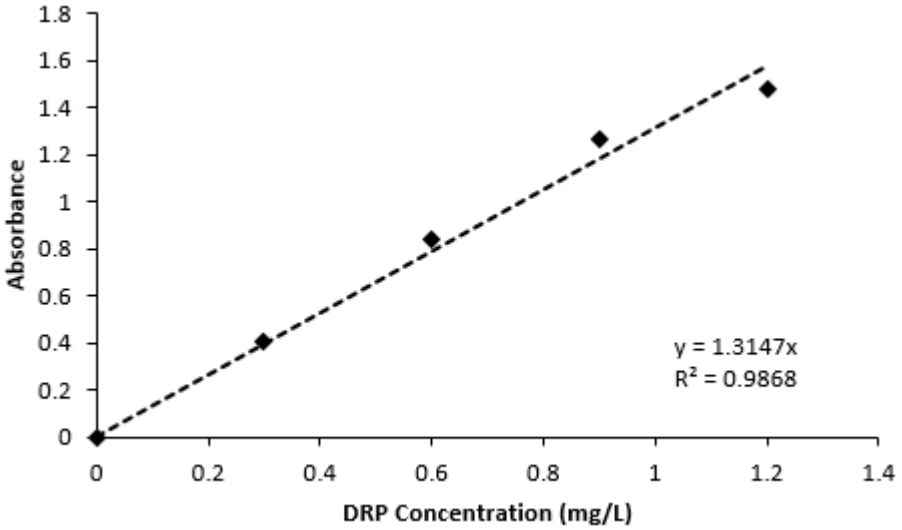


Figure 2.3: Calibration curve 2 for DRP. Cuvette had path length of 2 cm.

For each sample, from each site, different DRP analyses were carried out including a sample for each site for both rounds of sampling, a combined reagent blank, and a sample blank (sample with no reagent added) (Table 2.6).

Table 2.6: Sample reagent blanks and sample blanks (µg/L) from DRP analysis.

Well	Combined Reagent Blank		Sample Blank	
	April	July	April	July
1A	12.2	<9.45	16.7	13.7
1C	<9.45	<9.45	<9.45	<9.45
2A	4.94	3.39	3.39	<3.27
2C	4.94	3.39	6.17	3.39
3A	3.39	3.39	<3.27	<3.27
3C	3.70	<3.27	4.32	5.55
4A	14.7	7.71	12.6	8.02
4C	<3.27	<3.27	3.39	<3.27
5A	<3.27	<3.27	<3.27	<3.27
5C	<3.27	<3.27	<3.27	<3.27
6A	4.63	4.01	10.2	7.71
6C	4.01	<3.27	<3.27	<3.27
7A	13.3	9.25	16.0	15.4
7C	4.01	<3.27	4.63	<3.27
8A	6.79	<3.27	<3.27	<3.27
8C	<3.27	<3.27	3.70	<3.27
9A	<3.27	<3.27	4.32	<3.27
9C	<3.27	<3.27	4.63	<3.27

Combined reagent blanks were used as a baseline for each sample to determine DRP concentration from the combined sample reagent. The tubes of samples and blanks were prepared at 30 second intervals, in sets of 30, and were then tested at 30 second intervals. The detection limit for DRP is 0.0033 mg/L for the 5 cm pathlength cuvette and 0.0095 mg/L for the 2 cm pathlength cuvette.

2.5.5 Total, Inorganic, and Organic Carbon

Total and inorganic carbon were analysed in the Special Purposes laboratory of the Chemical and Process Engineering Department at the University of Canterbury. The Shimadzu TOC-L CSH analyser (liquid) had a working range of 4 μg/L to 30,000 mg/L and was calibrated for total carbon using a series of standard solutions of potassium hydrogen phthalate (KHP). The stock KHP solution (1000 mg/L) was made by dissolving 2.125 g of KHP in ultrapure

water and carrying out dilutions. The concentrations of the standard total carbon solutions were as follows: 0 mg/L, 2 mg/L, 4 mg/L, 8 mg/L, 16 mg/L, 32 mg/L, and 64 mg/L. The calibration curve for total carbon had an R^2 value of 0.9986.

The Shimadzu TOC-L CSH analyser (liquid) was calibrated for total inorganic carbon using a series of standard solutions of sodium carbonate and sodium bicarbonate. The stock solution, 1,000 mg/L TIC, was made by dissolving 3.497 g of sodium bicarbonate and 4.412 g of sodium carbonate in ultrapure water. The standard solutions of total inorganic carbon had the following concentrations: 0 mg/L, 2 mg/L, 4 mg/L, 8 mg/L, 16 mg/L, 32 mg/L, and 64 mg/L. The calibration curve for total inorganic carbon had an R^2 value of 0.9999. To analyse the total carbon and TIC, 8 mL of each sample was placed in the auto-sampler and the instrument set up to measure these compounds based on the above calibration curves. The concentration of total organic carbon was determined by subtracting the concentration of total inorganic carbon from the TC. The detection limit for TC and TIC was 0.05 mg/L.

2.6 Quality Control and Error Estimates

2.6.1 Analysis of Duplicates

For the ICP-MS analyses, an analytical duplicate was included after every ten samples. These duplicates included filtered and unfiltered samples as well as environmental blanks (Appendix 5). The mean percentage difference of the duplicates tested for As was 6.9%. Analytical duplicates and to a certain extent triplicates were used during total carbon and total inorganic carbon analyses. Each sample was tested twice and triplicates were run when the difference between the duplicates was high.

2.6.2 Analysis of Blanks

Effects of Acidification

The ultrapure water from the clean room laboratory was analysed, both unacidified and acidified, to determine whether the ultrapure acid may contain any trace elements that would contaminate the samples or whether the environmental blanks may have contained any trace elements from the deionised water. Most of the results were lower than the

detection limits and are not presented. There did not appear to be any particular difference between the filtered deionised water results and the results from the unfiltered deionised water (Table 2.7). This suggested that the syringe and 0.45 µm filter used in the clean room did not introduce any particular trace elements to the deionised water. The blanks showed that the acid may introduce trace amounts of Ca, Fe and Al.

Table 2.7: Results of ICP-MS analysis on ultrapure water, both filtered and unfiltered, acidified and not acidified (µg/L).

Analyte	Unfiltered deionised water	Unfiltered acidified deionised water	Filtered deionised water	Filtered acidified deionised water
Na	11.0	13.6	11.6	13.6
Al	<1.0	1.7	<1.0	1.8
Ca	<10.0	18.6	<10.0	42.8
Fe	<1.0	3.2	<1.0	1.5

Sampling Apparatus Blank

To obtain a blank from the sampling apparatus, ultrapure water was run through the sampling apparatus, then collected and analysed. One shortcoming of this analysis is that water was run through the sampling apparatus for at least fifteen minutes in the field prior to sample collection, whereas only three litres of ultrapure water was used for this analysis. The higher water pressure in the field may have dislodged solid particulates in the sampling apparatus prior to sample collection, resulting in less contamination than is present in the blank (Table 2.8). From the sampling apparatus blank, the total concentrations of chemicals was higher than dissolved concentrations which suggests that the contamination is being introduced via particulates from the sampling apparatus.

Syringe Blanks

Two types of syringes were used during sampling: Monoject 60 mL syringe and Chirana 23 mL syringe. These syringes and filters may have been a source of contamination, so ultrapure water was filtered through the syringes to collect blanks (Table 2.8). These blanks were prepared in the water laboratory at Lincoln University.

There was slightly more contamination from the Chirana syringe for Na, K, Ca, Fe, Ni and Cd. The Monoject syringe introduced more Zn contamination to water than the Chirana syringe.

Table 2.8: Chemical composition of ultrapure water blanks filtered through two types of syringes and the sampling apparatus (µg/L).

Parameter	Chirana 23 mL Syringe	Monoject 60 mL syringe	Unfiltered Ultrapure Water	Filtered sampling apparatus blank	Unfiltered sampling apparatus blank
Na	21.4	13.0	11.0	<10.0	13.9
K	18.4	10.6	<15.3	<15.3	<15.3
Al	<1.0	<1.0	<1.0	<1.0	2.06
Ca	84.4	55.3	<10.0	72.9	102
Fe	1.46	<1.0	<1.0	1.03	24.6
Mn	<0.1	<0.1	<0.1	0.227	0.772
Ni	0.159	<0.1	<0.1	0.700	3.27
Cu	<1.0	<1.0	<1.0	2.33	101
Zn	4.20	8.14	<10.0	37.1	183
Pb	<0.1	<0.1	<0.1	0.124	4.27
Cd	0.379	<0.1	<0.1	<0.1	0.527

Environmental Blanks

Environmental blanks consisted of ultrapure water that was exposed at the site for several minutes (Table 2.9). The first round of sampling at site 6A was windy and raining, which may have influenced the results. Many of the analytes measured were below the accurately detectable limits. However, the environmental blank from well 6A in the first round of sampling had detectable levels of most trace elements. For the second round of sampling, there was detectable Na, Ca, Mn and Fe at well 1A, detectable Na, Ca, Fe and Pb at well 3A, detectable Ca at well 5A, detectable Na, Ca, Mn, Fe, Cu and Pb in well 7A, and detectable Na, K and Ca in well 9A. The As concentration was below the detection limit for every environmental blank.

Table 2.9: Chemical composition of the environmental blanks (µg/L). NT = not tested.

Blanks	1A	3A	5A	6A	7A	9A
NO_3	NT	NT	NT	205	NT	NT
DRP	NT	NT	NT	5.31	NT	NT
Na	17.8	15.9	<10.0	121	18.1	37.8
Mg	<10.0	<10.0	<10.0	22.2	<10.0	<10.0
K	<15.3	<15.3	<15.3	72.6	<15.3	19.5
Ca	31.8	35.0	21.1	251	31.4	44.8
Mn	0.106	<0.1	<0.1	0.534	0.115	<0.1
Fe	3.29	1.48	<1.0	3.85	3.53	<1.0
Al	<1.0	<1.0	<1.0	3.58	<1.0	<1.0
Cu	<1.0	<1.0	<1.0	3.14	0.986	<1.0
Zn	<10.0	<10.0	<10.0	29.0	<10.0	<10.0
Pb	<0.1	0.279	<0.1	0.167	0.716	<0.1
Cd	<0.1	<0.1	<0.1	0.550	<0.1	<0.1
Ni	<0.1	<0.1	<0.1	0.996	<0.1	<0.1

2.6.3 Minimising Sample Contamination

Contaminants can be introduced into the samples in the field but steps were taken to minimise the risk of this occurring. The well was purged prior to sampling so that the water sampled would be representative of the groundwater and not altered by the condition of the bore. Nitrile gloves were worn during sampling so that contamination from skin was minimised and hands were sanitised before putting on the gloves. The syringe was rinsed with distilled water prior to sampling, then rinsed again three times with water from the well. All sample tubes were sealed in separate ziplock bags prior to sample collection and then double-bagged following sample collection. Syringes were also kept sealed in ziplock bags. At the beginning of the filtering process, 10-20 mL of water from the well was pushed through the filter to clean the filter before sample collection began. For unfiltered samples, the centrifuge tubes were rinsed with sample water prior to collection. The sampling apparatus was used whenever possible to minimise the differences between samples from different wells. However, it was not always possible to use the multi-tap equipment.

2.6.4 Analytical Error Calculation

Error can be introduced during experimental procedures. During acidification, the samples were briefly exposed to the air. However, acidification was carried out in a clean room Environment, inside a fume hood, to minimise contamination. Error could have been introduced during sample preparation for HPIC and ICP-MS if dilutions were inaccurate but automatic micropipettes and scales were used to ensure that the volumes used in the dilutions were as accurate as possible. The samples were processed very little. However, for DRP, total carbon and IC, stock solutions and reagents were made and diluted to standard solutions, which added a greater element of error. The error associated with each instrument or piece of equipment was different (Table 2.10). The percentage error for each analysis was calculated by dividing the error for each tool by the volume/mass measured, summing the error for each analysis in this way, and multiplying by 100. The percentage error ranged from 0.06% for undiluted ICP-MS samples to 30.1% for DRP samples.

Table 2.10: Errors for instruments used during analysis.

Instrument	Error
1 mL Auto Pipette	0.0005 mL
Scales	0.00005 g
1 L Volumetric Flask	0.3 mL
100 mL Volumetric Flask	0.08 mL
Shimadzu TOC-L CSH analyser (liquid)	0.0005 mL
5 mL Auto Pipette	0.0025 mL
DIONEX ICS-2100 HPIC Instrument	0.0005 mL
10 mL Graduated Cylinder	0.38 mL
500 mL Volumetric Flask	0.2 mL
250 mL Volumetric Flask	0.12 mL
50 mL Volumetric Flask	0.05 mL
50 mL Graduated Cylinder	0.5 mL
10 mL Volumetric Flask	0.02 mL
25 mL Graduated Cylinder	0.3 mL

Instrumental Error

Instrumental error was calculated by determining the percentage difference between analytical duplicates for each well that had an analytical duplicate (Equation 2.5). The mean percentage error was 6.9%.

Equation 2.5 $$Percentage\ difference = \frac{\Delta Concentration}{Mean\ Concentration} \text{ x } 100$$

Instrumental error was calculated a second way by determining the percentage recovery of the Certified Reference Material. The round 1 percentage recoveries ranged from 99.8% for Na to 115.9% for Fe. The round 2 percentage recoveries ranged from 97.4% to 134.9%.

Sampling Error

Sampling error was calculated by determining the percentage difference between sample duplicates for each well from which they were collected (Equation 2.5). The percentage difference between duplicates ranged from 0.0% to 16% and the average was 4.2%.

2.6.5 Major Ion Balances

The ion balance was determined for each well to test completeness and accuracy of major ion analyses (Equation 2.6). All ion balances were <10% except for the following for round 1: 4C (-16.8%), 5C (-16.9%), 6A (-15.2%), and 8C (25.8%). For round 2, all ion balances were <10%.

Equation 2.6 $$IB(\%) = \frac{\Delta cations - anions\ (moles) x\ Charge}{Total\ ions\ (moles)} \text{ x } 100$$

2.6.6 PHREEQC Geochemical Modelling

PHREEQC is a computer modelling programme that is used to carry out aqueous geochemical calculations (Parkhurst & Appelo, 2013). PHREEQC can be used to determine speciation, surface complexation, ion-exchange equilibria, mixing of solution, and transport, amongst other factors (Parkshurst & Appelo, 2013). The measured concentrations of all analytes were entered into PHREEQC with physicochemical characteristics such as pH and temperature. This was then used to model the condition in each individual well, in particular looking at the saturation indices for minerals to determine what minerals may precipitate from groundwater.

Chapter 3

Analysis of Environment Canterbury Groundwater Data

In this chapter, the results from the statistical analysis of Environment Canterbury's groundwater monitoring data are presented. The database was analysed to identify key relationships between arsenic (As) concentration and ground water physicochemical characteristics and well properties.

3.1 Environment Canterbury Sampling

Since 1990, Environment Canterbury have tested 459 wells to determine As concentration. Many of these wells were tested only once for As. The majority of the wells with ongoing testing are sampled annually, and six wells with detectable As concentrations are, or were previously, tested quarterly. Eight other wells were tested more than once in a year, but in no particular pattern. The detection limit for the majority of these As tests was 0.002 mg/L. The number of wells used for each analysis varied depending on the number of wells in which both As and other variables have previously been tested (Table 3.1). For instance, 459 wells were tested for As, but only 435 of these were also tested for iron (Fe) and manganese (Mn).

Table 3.1: Number of Environment Canterbury monitoring wells involved in each type of analysis.

Analysis	Number of wells	Analysis	Number of wells
GIS arsenic (As)	459	Arsenic correlations with iron and conductivity	29
GIS iron (Fe) and GIS manganese (Mn)	435	Arsenic correlation with manganese	28
GIS dissolved organic carbon (DOC)	46	Arsenic correlation with sulfate	26
GIS sulfate (SO_4)	397	Arsenic correlation with dissolved reactive phosphorus (DRP)	21
GIS dissolved oxygen (DO)	366	Arsenic correlation with copper (Cu)	20
Depth	428	Arsenic correlation with chromium (Cr)	19
Temporal	16	Arsenic correlation with nitrate (NO_3)	14
Arsenic correlations with calcium (Ca) and chloride (Cl)	30	Arsenic correlation with cadmium (Cd)	12

3.2 GIS Mapping

Geographical Information Systems (GIS) were used to map the available Environment Canterbury data for dissolved As, dissolved Fe, dissolved Mn, dissolved organic carbon (DOC), and sulfate (SO_4). These parameters were selected as their relationships with As are often used to elucidate the most likely mechanism of As release into groundwater. A total of 459 wells were included in the GIS analysis. These were the wells that had previously been tested for As by Environment Canterbury. Not all of these wells were tested for every other parameter, so the total number of wells for each parameter was not the same. Where a concentration was less than the detection limit, a value of half the detection limit was used for mapping. The detection limits were for As (0.002 mg/L), Fe (0.03 mg/L), Mn (0.01 mg/L), DOC (0.1 mg/L), and SO_4 (0.1 mg/L). Concentrations were colour-coded, with the highest concentrations in red, decreasing to orange, yellow, green, with the lowest concentration in blue and purple.

3.2.1 Arsenic Distribution

The distribution of As in Canterbury groundwater was patchy and irregular (Figure 3.1). The concentration of As ranged from <0.002 mg/L to 0.9 mg/L, with the highest concentrations of As (0.1 – 0.9 mg/L) in Kaikoura and north of Christchurch. Elevated-As wells did not appear in inland Canterbury. Of the 459 wells with As tested, 64 had detectable As. Hotspots of elevated As in groundwater were also located south of Timaru, near Twizel, on the Brighton/Southshore spit. These hotspots were primarily in coastal areas which contrasts with results found by Ministry of Health (2002), where As in New Zealand groundwater was determined not to be any higher in coastal wells (within 2 km of coast) than those further inland. The research by the Ministry of Health (2002) involved a set of 45 wells within 2 km of the coast and data from a larger dataset of 121 groundwater wells.

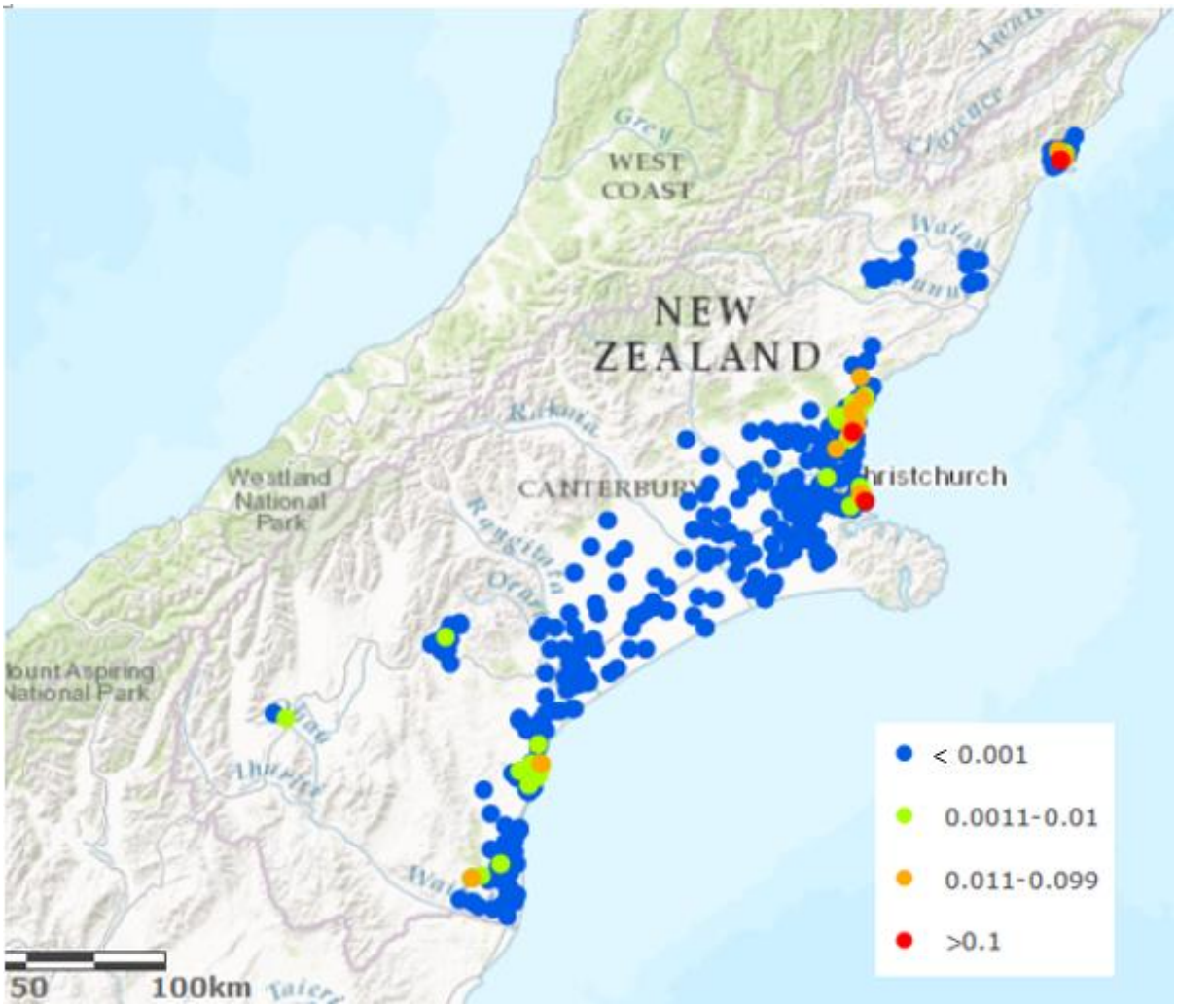


Figure 3.1: Map showing the distribution of dissolved As in Canterbury wells, produced using ArcGIS Online (number of wells, n = 459).

3.2.2 Iron Distribution

The distribution of Fe in Canterbury groundwater was more regular than the distribution of As (Figure 3.2) and 397 wells of the 436 tested had detectable Fe. The concentration of Fe ranged from <0.03 mg/L to 200 mg/L, with the highest Fe concentrations (20 – 200 mg/L) occurring to the east of Waikuku and Woodend, with hotspots occurring at Timaru and near the mouth of the Waitaki River. Elevated Fe in groundwater was located inland of Christchurch and in Kaikoura. Most of these hotspots correspond to As hotspots, with the exception of the Brighton/Southshore spit (where As concentration is elevated but not Fe concentration), and inland Christchurch (where Fe concentration is elevated but As concentration is not).

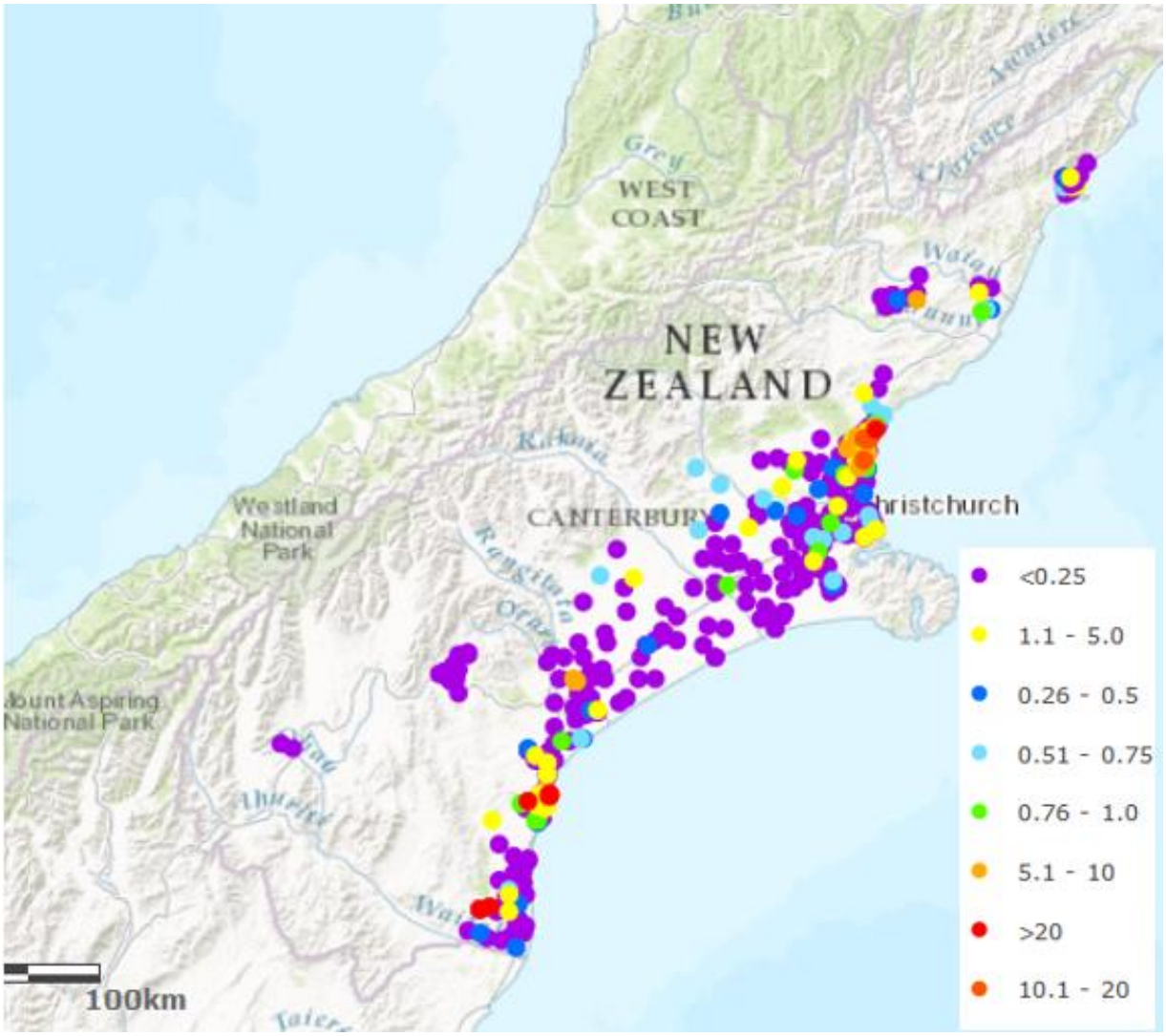


Figure 3.2: Map produced with ArcGIS Online showing the distribution of dissolved Fe in Canterbury wells (n = 435).

3.2.3 Manganese Distribution

Manganese was detected in 421 of the 435 wells where it was tested (wells that were also tested for As). The concentration of Mn ranged from <0.001 to 54 mg/L and was elevated in coastal wells, with the highest concentration (1 – 54 mg/L) at Timaru, the lower Waitaki area, and east of Waikuku and Woodend (Figure 3.3). Hotspots of groundwater with elevated Mn concentrations were also located in Kaikoura, and north of the Hurunui River. Elevated Mn appeared to correspond to elevated As and Fe concentrations in Canterbury.

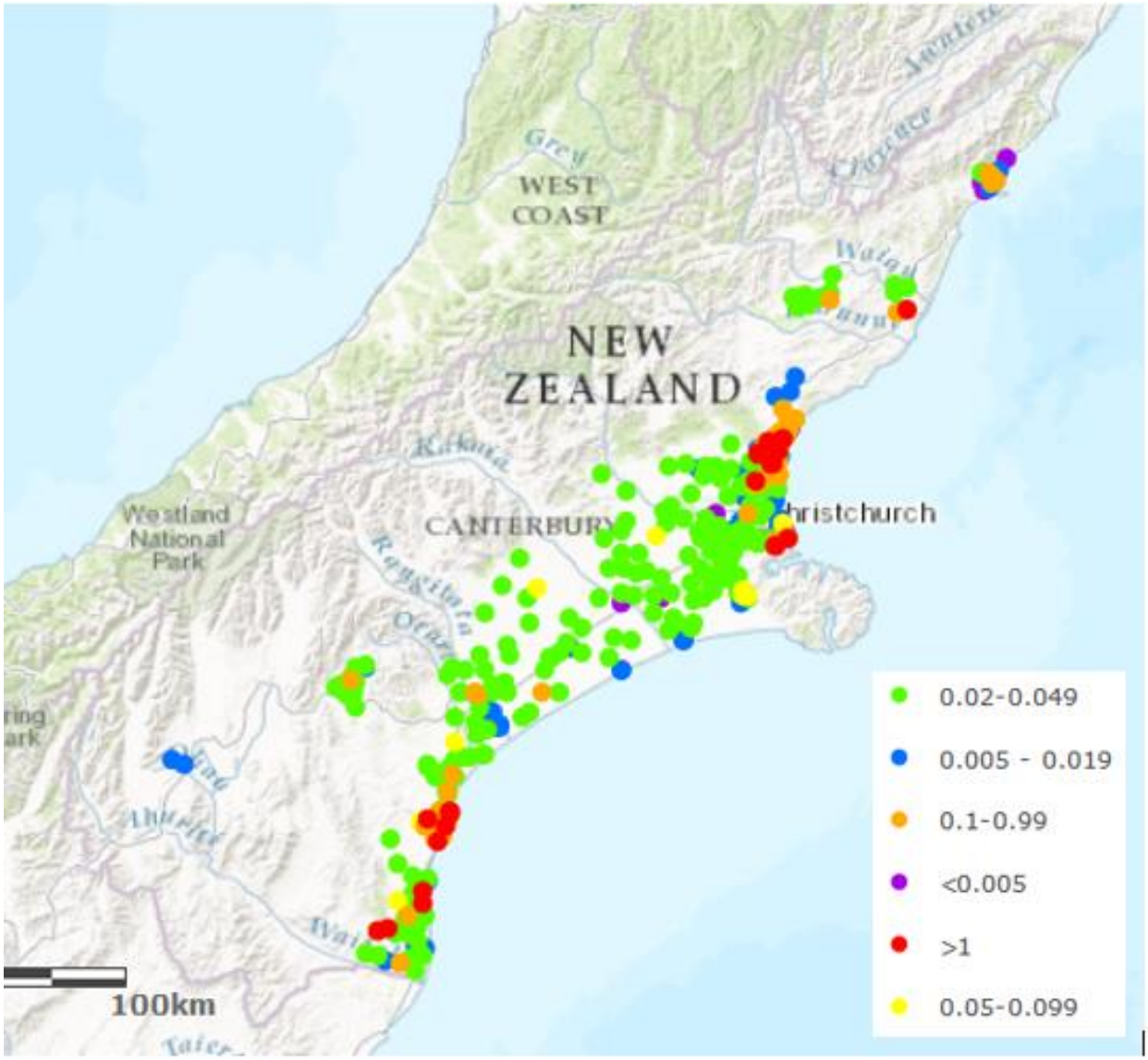


Figure 3.3: Map showing the distribution of dissolved Mn in Canterbury groundwater at wells where As has been tested for (n = 435).

3.2.4 Organic Carbon Distribution

The concentration of dissolved organic carbon (DOC) ranged from 0.1 to 6.18 mg/L. The distribution of DOC was variable, with the highest concentrations (5.0 – 6.18 mg/L) north of Christchurch, at coastal Christchurch and Rangitata (Figure 3.4). DOC concentrations were also elevated in wells located in Ohoka and Kaikoura. Only the hotspot in Kaikoura corresponded with hotspots for other parameters. Elevated DOC concentrations were measured at both inland and coastal wells.

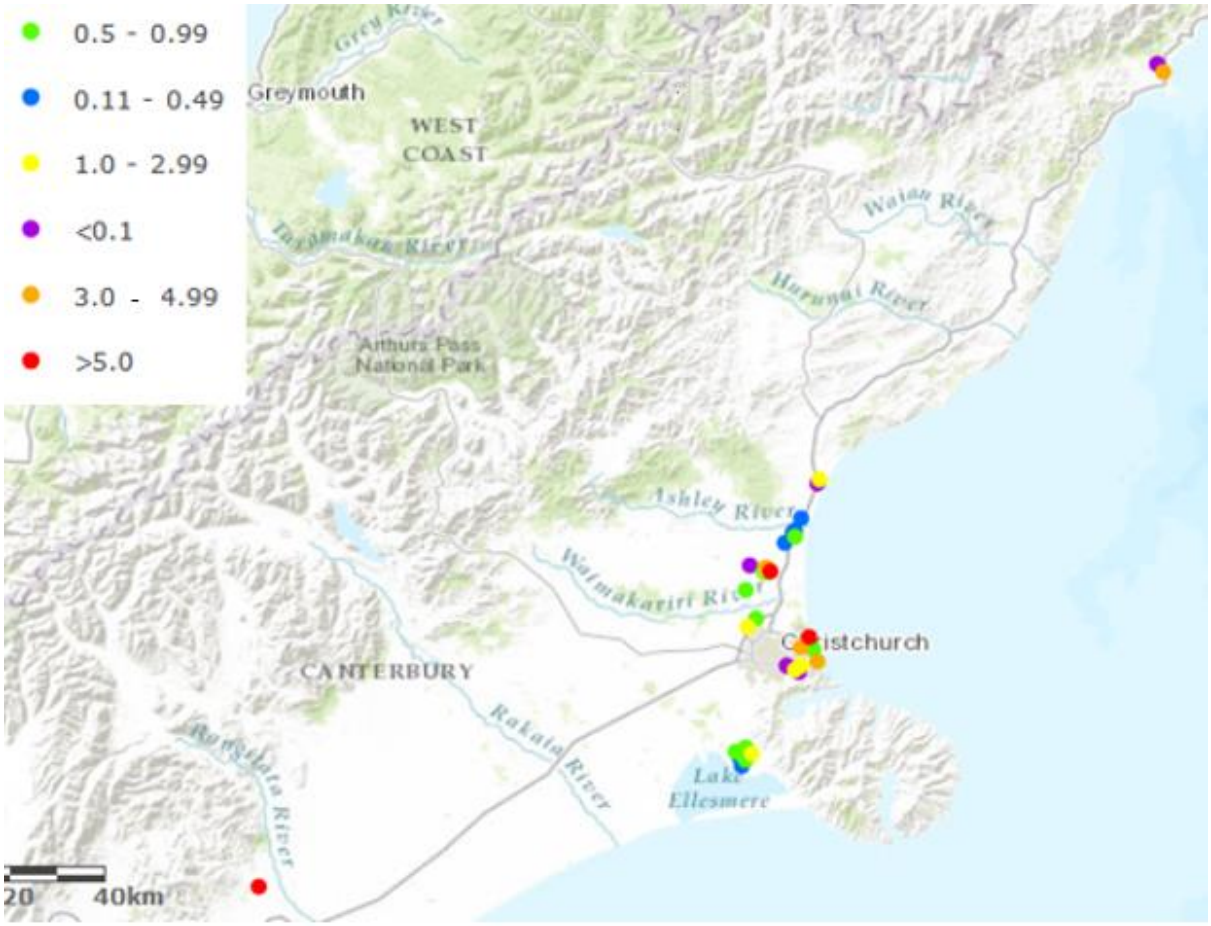


Figure 3.4: ArcGIS Online map showing the distribution of dissolved organic carbon in Canterbury at wells where As has been tested for (n = 46).

3.2.5 Sulfate Distribution

Sulfate was detectable in 396 wells of the 397 wells where it was measured and the concentration ranged from 0.1 to 2,000 mg/L (Figure 3.5). Wells with elevated SO_4 concentrations (50 – 2,000 mg/L) were located in Kaikoura, near the mouth of the Waiau, north of Christchurch, in the Avon-Heathcote estuary area, Timaru, and in the lower Waitaki area. South Canterbury had moderate to high concentrations of SO_4 while Mid Canterbury had lower concentrations. The hotspots near Rangiora and the Waitaki River did not correspond with hotspots for Fe, Mn or As. Elevated SO_4 was present in both coastal and inland wells.

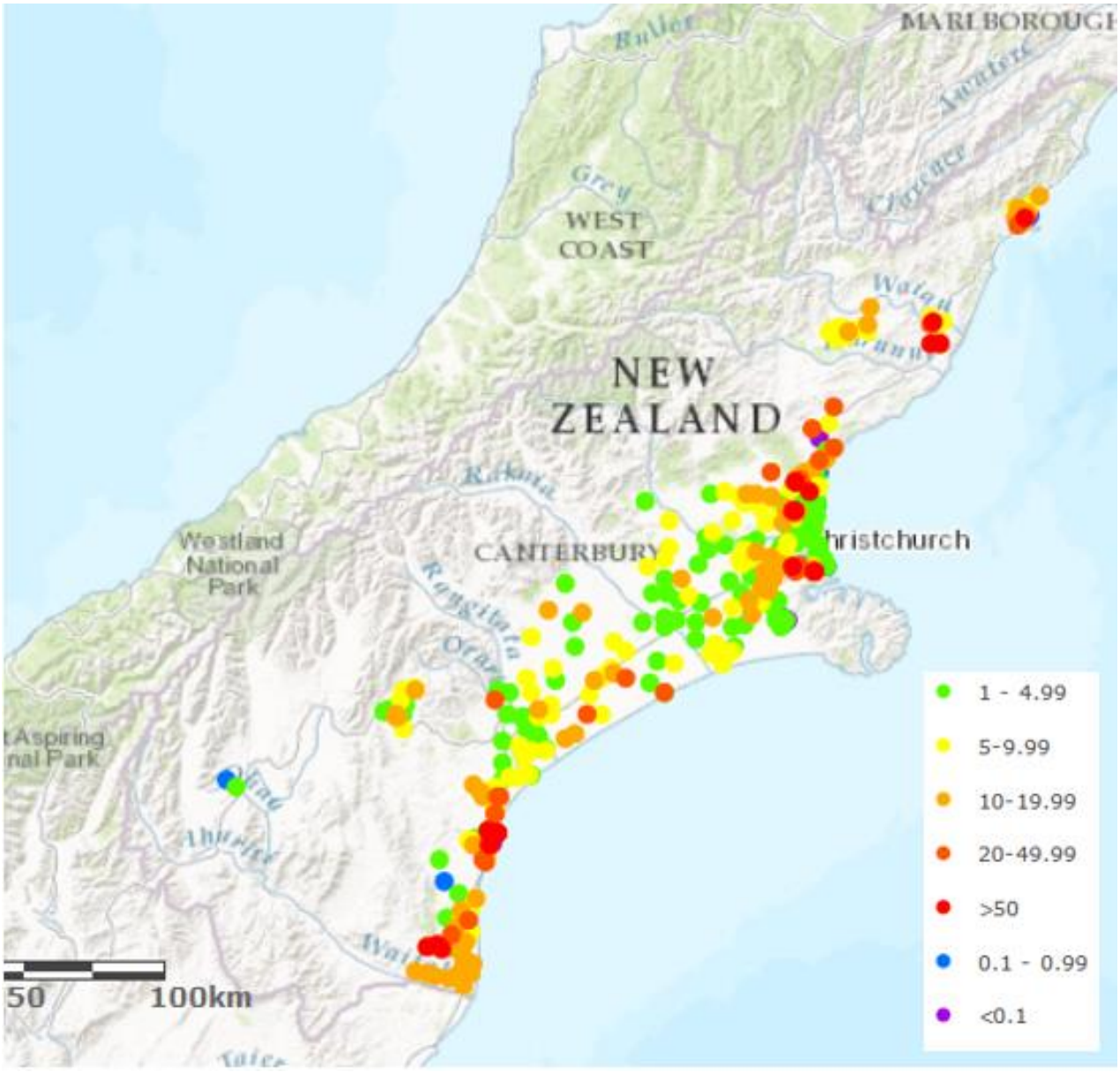


Figure 3.5: Distribution of dissolved SO_4 in Canterbury at wells where As has been tested for (n = 397).

3.2.6 Dissolved Oxygen Distribution

Dissolved oxygen (DO) concentrations were regularly distributed across Canterbury and ranged from 0.04 mg/L to 13.43 mg/L (Figure 3.6). The highest DO concentrations were at western Christchurch, north of Timaru, and Kaikoura. These wells were both coastal and inland.

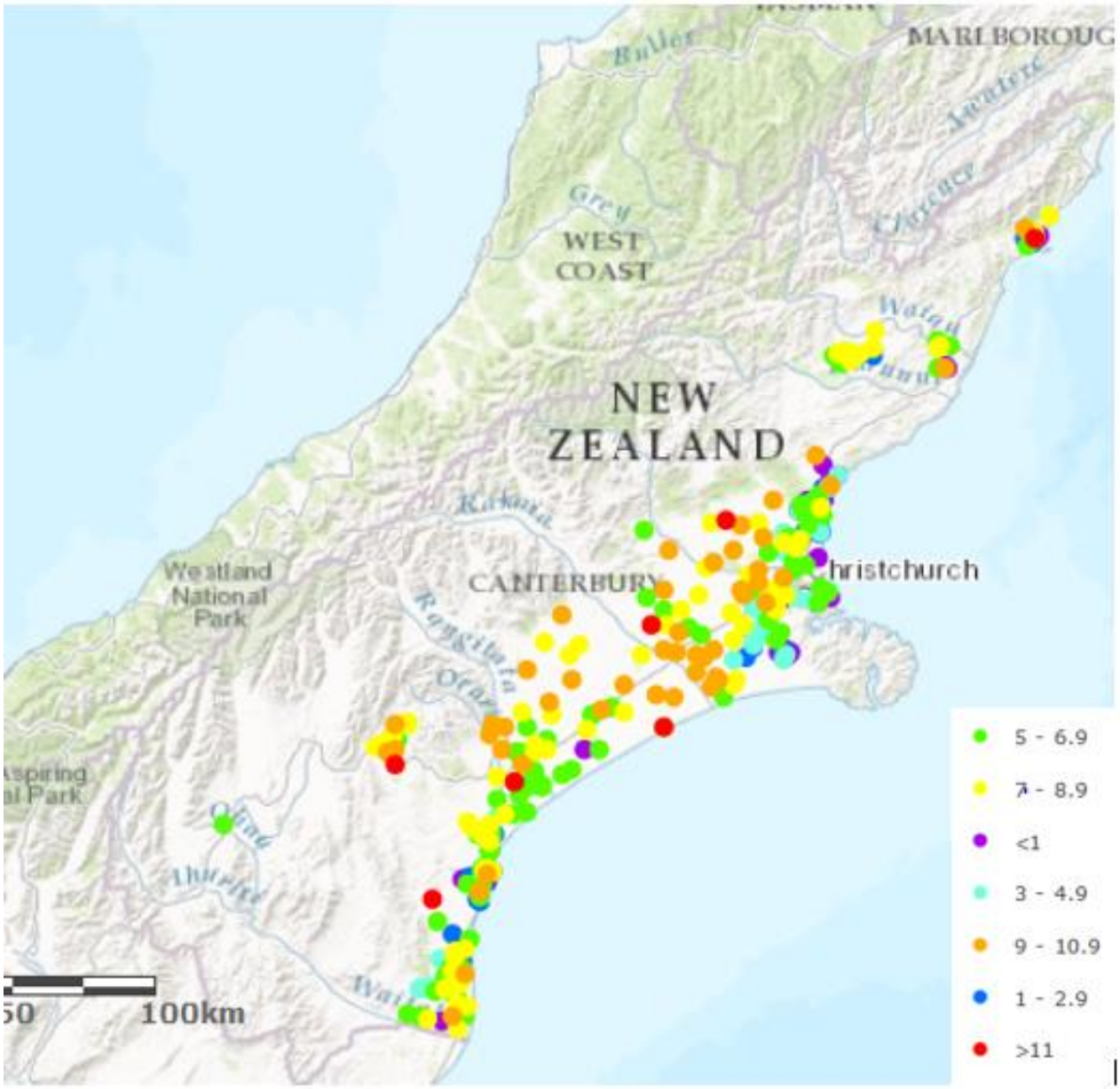


Figure 3.6: ArcGIS Online map showing the distribution of dissolved oxygen in Canterbury at wells where As has been tested for (n = 366).

3.2.7 Physicochemical Distribution Summary

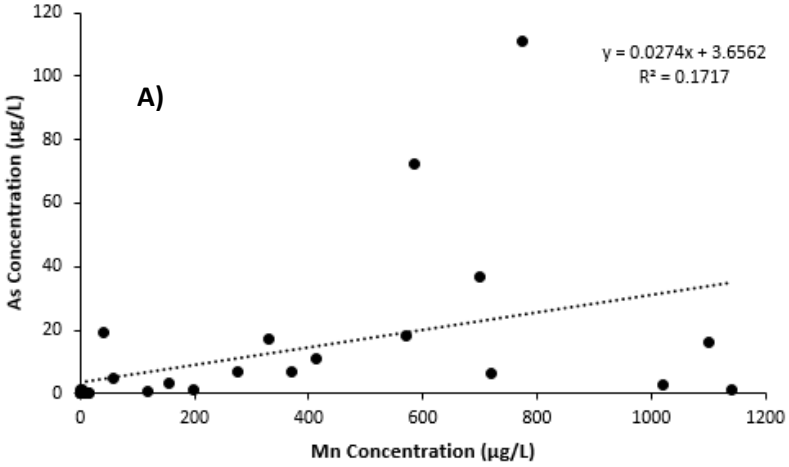
Hotspots for As and Mn were primarily coastal while the other parameters had hotspots in both inland and coastal areas. The fact that Mn also had higher concentrations in coastal areas than inland areas may indicate that chemicals tend to accumulate in the coastal area which is effectively the most 'downstream' groundwater gets before eventually seeping into the ocean. Southern Timaru had elevated concentrations of Fe, Mn and SO_4 in groundwater.

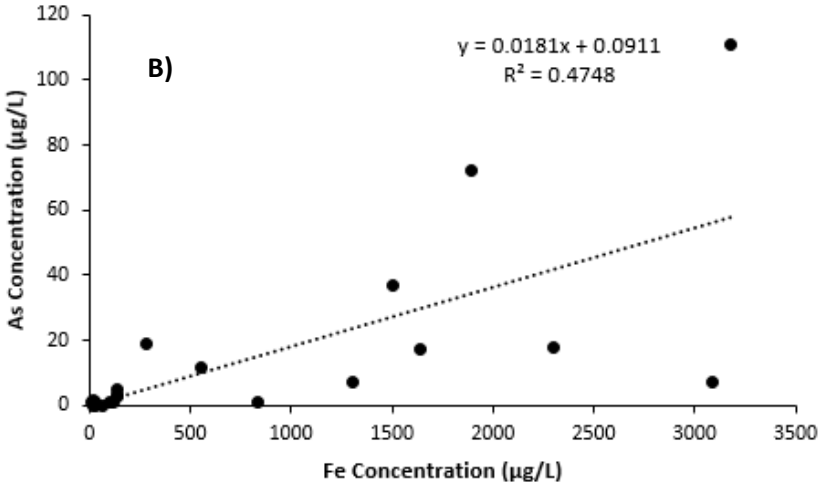
3.3 Relationships between Arsenic and Physicochemical Characteristics

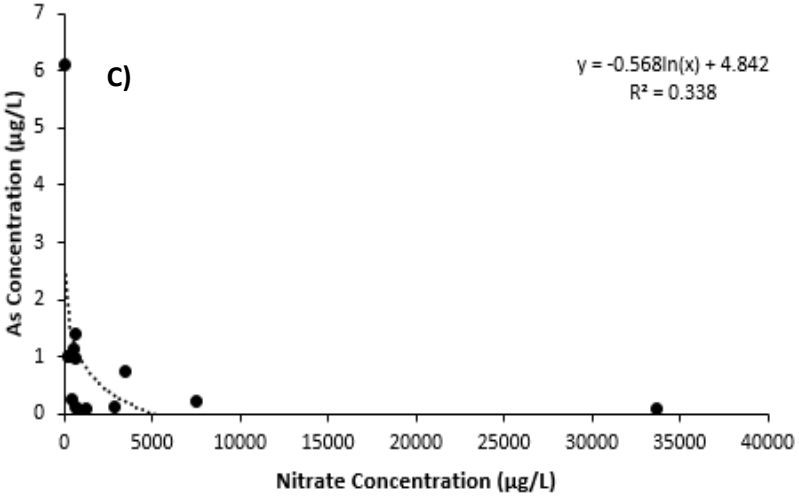
Scatter graphs were plotted to determine whether there were linear correlations or other relationships between the concentrations of As and other parameters including Fe, Mn, DO, SO_4 and nitrate (NO_3). Only detectable results are shown (Table 3.2). T-tests were carried out to compare the concentration of a chemical in wells with detectable arsenic to the concentrations of the chemical in wells where As was below the detection limit (0.002 mg/L). The *p*-value for Pearson's correlation coefficient was also calculated.

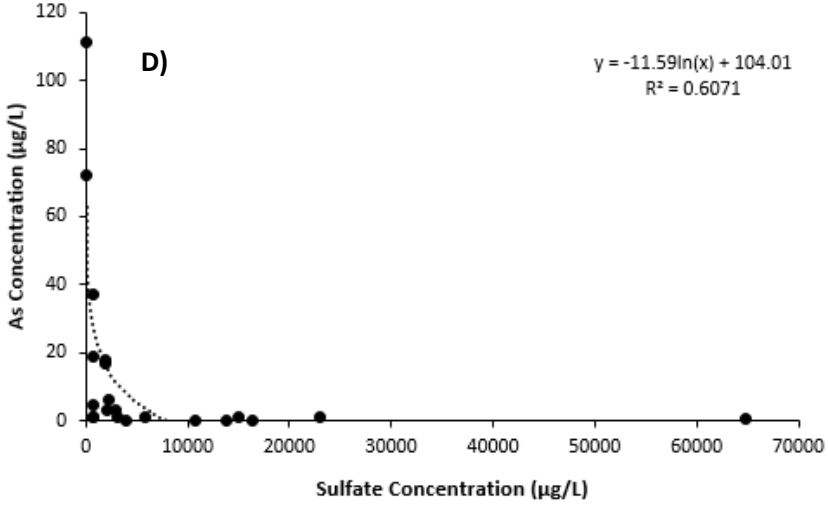
Table 3.2: Detection limits for each chemical which was plotted against arsenic, p-values and number of wells included. NA = not applicable.

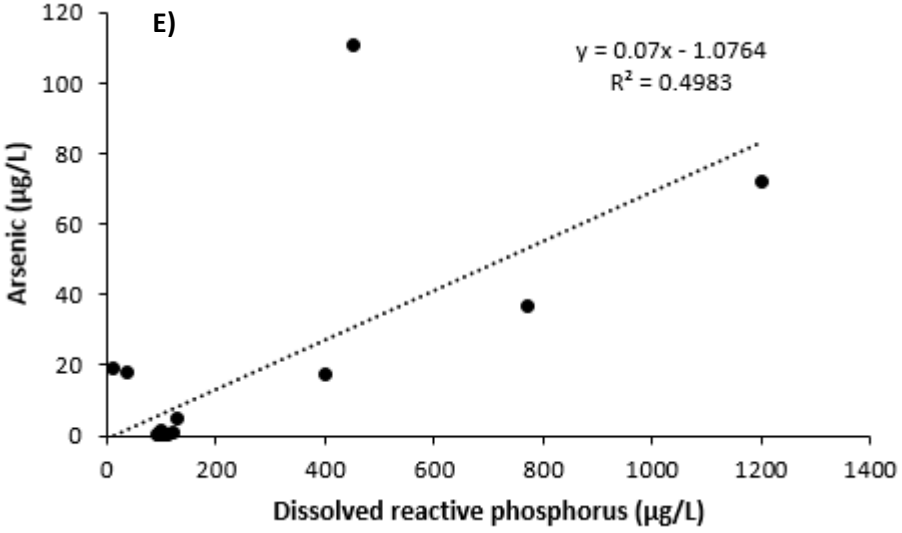
Chemical	Detection Limit (mg/L)	*P*-value of correlation with As	Number of wells
As	0.002	NA	NA
Mn	0.01	0.028	28
Fe	0.03	0.000036	28
NO_3	0.1	0.45	14
SO_4	0.025	0.23	26
DO	NA	0.79	46
DRP	0.001	0.00035	21



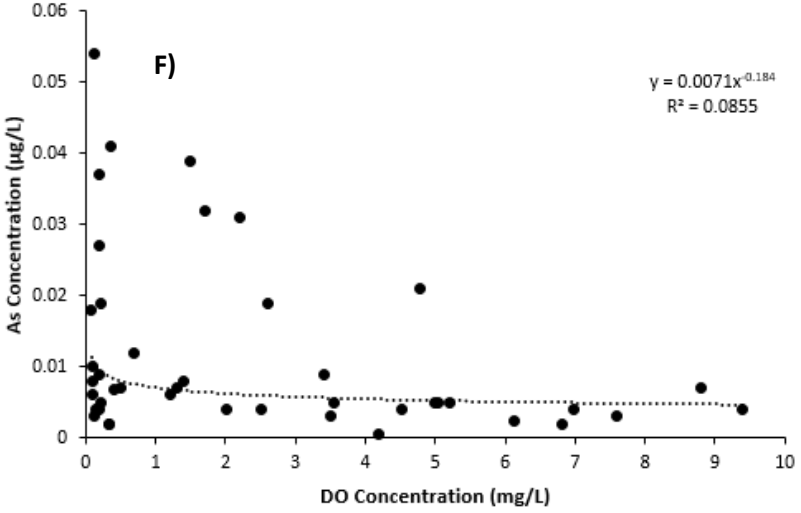








Figures 3.7 A - F: Correlation of dissolved As with Mn (A), Fe (B), NO3 (C), SO4 (D), dissolved reactive phosphorus (E) and DO (F).



Iron and Manganese

Dissolved As and Mn were correlated (p<0.05) (Figure 3.7A). The relationship between As and Fe was significant when an outlier with extremely high Fe was removed (p<0.05) (Figure 3.7B). The Mn and Fe concentrations in wells with detectable As were significantly greater than in wells with no detectable As. The significant relationships between As and Mn, and Fe and As, were inconsistent with the results of the study of New Zealand coastal groundwaters by the Ministry of Health (2002), but consistent with the study of Waikato groundwater by Environment Waikato (2006). The latter study considered the results to be consistent with release of As under reducing conditions (in which amorphous Fe and Mn oxides dissolved). The correlation found between Mn, Fe and As was also consistent with studies in Bangladesh, Serbia and West Bengal which found high concentrations of Mn and Fe in wells with elevated As concentrations (Smedley, 2003) (Katsoyiannis, 2014).

Nitrate

There was no significant correlation between As and NO_3 concentrations in groundwater (Figure 3.7C). The relationship resembled mutual exclusion, but a t-test revealed no significant difference in As concentration in wells with NO_3 concentrations ≤0.5 mg/L compared to those >0.5 mg/L. The lack of significant relationship was not consistent with research by the Ministry of Health (2002) which found that elevated As concentrations were found more often in New Zealand wells with low nitrate concentrations, and also contrasted to a study by Environment Waikato (2006) who found a highly significant negative correlation between As and NO_3-nitrogen in Waikato wells. It was considered that the Ministry of Health's (2002) findings may indicate a link between elevated As concentrations and reducing conditions.

The lack of relationship between NO_3 and As concentrations was inconsistent with a previous overseas study which determined that reducing groundwaters with elevated As concentrations in West Bengal had low concentrations of NO_3 (Smedley, 2003). In contrast, Giménez-Forcada and Smedley (2014) reported that wells with elevated As concentrations in the Duero Basin of Spain were generally oxidising and alkaline with high nitrate concentrations and that the most likely mechanism of release into groundwater was the

oxidation of arsenic-bearing sulfide minerals. Nicolli et al (2012) found similar chemical relationships in the groundwaters of the Salí River Basin, Tucumán Province, Argentina.

Sulfate

Arsenic and SO_4 were not significantly linearly correlated (Figure 3.7D), but there was a weakly logarithmic relationship, showing mutual exclusion. There was a significant difference in As concentration in wells with ≤3 mg/L SO_4 compared to wells with >3 mg/L SO_4; wells with higher SO_4 concentrations had significantly lower As concentrations (*p*-value of 0.044). This finding was consistent with a study by Environment Waikato (2006) which found a very significant correlation between As and SO_4. They inferred that the correlation indicated that As was present in more highly reducing wells where As was released from sulfide minerals as well as Mn and Fe oxides (Environment Waikato, 2006). It was also consistent with studies in West Bengal which found low concentrations of SO_4 in groundwaters with elevated concentrations of As, and a study in the Huhhot Basin of Inner Mongolia (Smedley, 2003). These studies found low concentrations of SO_4 occurring in wells with elevated concentrations of As, as a result of the reducing conditions which led to reduction of SO_4 to form sulfides as well as the release of As (Smedley, 2003).

Dissolved Reactive Phosphorus

There was no significant difference in the concentration of dissolved reactive phosphorus in wells with detectable As compared to those with no detectable As (*p*-value of 0.20), but they were positively correlated ($p<0.05$) (Figure 3.7E). This was one of the strongest correlations measured and was consistent with the results from a study by Anawar et al (2011) which found a strong correlation between the concentration of As and phosphate in shallow tubewells in Bangladesh. The strong positive correlation may be because phosphate and arsenate are structural analogues and adsorb to similar sorption sites on minerals. Phosphate can release arsenate (Figure 3.8) from Fe oxides via anion exchange because they compete for the same surface adsorption sites (Zeng et al., 2008). This was the case in a study by Stollenwork et al which found that increasing concentrations of P(V) caused decreased adsorption of As(V) to ferrihydrite, a common Fe-based mineral (Stollenwerk, 2003).

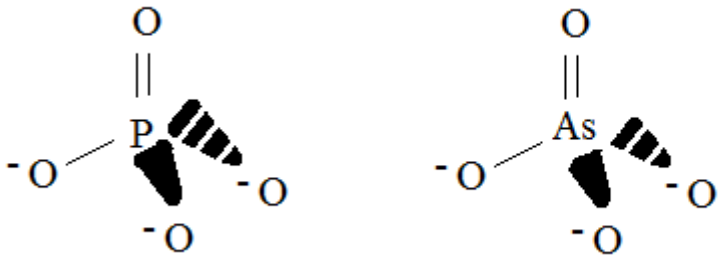


Figure 3.8: Structures of phosphate and arsenate.

Dissolved Oxygen

The concentration of DO was significantly lower in wells with detectable As than in wells with no detectable As (p<0.05) despite the lack of a significant linear correlation (Figure 3.7F). A t-test showed that As concentration was higher in wells with DO ≤4 mg/L than in wells with DO>4 mg/L (p<0.05). A mutually exclusive relationship was shown between As and DO concentrations which indicates that dissolved As primarily occurs in anoxic environments. This was consistent with research in the Bengal Basin which found that wells with elevated As predominantly had low DO concentrations (Ahmed et al., 2004). A study by Smedley et al (2007) found a weak negative correlation between DO and As concentration in wells in Burkina Faso. However, most As was present as As(V), and the concentrations of Fe and Mn were low, so it was determined that this correlation had less to do with As being released in anoxic environments, and more to do with the fact that DO decreased with depth, and As concentration was related to depth (Smedley et al., 2007). DO was simply a third variable which happened to be related to the causal variable, i.e. depth. It is possible that the relationship between As and DO in Canterbury groundwater is incidental, caused by a third variable. The majority of wells in Canterbury are moderately aerobic (x>3 mg/L) (Figure 3.6). This suggests that most As should be present as As(V) because As(III) is unstable in aerobic environments (Stollenwerk, 2003). However, the oxidation of As(III) occurs very slowly unless catalysed by the presence of other redox-sensitive species such as Fe and Mn oxides and light (Stollenwerk, 2003).

Dissolved Organic Carbon (DOC)

The linear relationship between As and DOC concentrations was not significant, but there was a significant difference between the DOC concentration in wells with detectable As

compared to wells with no detectable As (*p*-value of 0.031). This result was expected based on a review of literature which showed that wells with high organic carbon content would likely have elevated arsenic because the groundwater conditions would become reducing as organic matter was oxidised, whether chemically or microbially. It has previously been reported that groundwaters with elevated As had high concentrations of dissolved organic carbon (Ahmed et al., 2004). In Bangladeshi wells where the reductive dissolution mechanism occurs, high concentrations of organic matter were found and there was a strong correlation between As concentration and the concentration of organic matter (Smedley, 2003).

Other Parameters

Correlations were plotted for other parameters including Cd, Ca, Cl, Cr, and Cu with As, but none of these were found to be significant or to have a particular pattern. Interestingly, there was no correlation between As and conductivity, when studies internationally have found that As tends to be elevated in wells with higher conductivities (Kinniburgh et al., 2003).

3.4 Coastal/Inland Analysis

A series of t-tests were conducted to determine whether the As concentration was significantly different on different sides of an arbitrary line to define a coastal/inland distinction. Results indicated that the concentration of As was significantly higher in wells within 4.0 km of the coast than in wells further inland (Table 3.3). The difference in the concentration of As in coastal wells compared to inland wells remained significant until the 'boundary' was at 60 km from the coast ($p>0.05$) (Table 3.3). This result was partially in accordance with a study by Ministry of Health (2002) which found no significant difference in the detectability of As in wells within 2 km of the coast compared to those further inland. The current test also found no difference in the concentration of As in wells within 2 km of the coast to those further inland. However, the present study did find a difference in As concentration in wells 4.0 km from the coast compared to those further inland.

Table 3.3: P-values for the difference in arsenic concentration in groundwater between inland and coastal wells.

Definition of 'Coastal'	*P*-value	Significant difference?
≤ 1.0 km from the coastline	0.64	No
≤ 2.5 km from the coastline	0.098	No
≤ 4.0 km from the coastline	0.050	Yes
≤ 5 km from the coastline	0.049	Yes
≤ 30 km from the coastline	0.041	Yes
≤ 50 km from the coastline	0.046	Yes
≤ 60 km from the coastline	0.29	No

There are multiple possible reasons why coastal wells may have higher concentrations of arsenic than those further inland. Arsenic may accumulate as it flows slowly downstream and ends up in lower lying coastal areas. This was the case in a study by Ahmed et al (2004) found moderate to severe As enrichment in wells in depressed areas and flood hazard areas in the Bengal Basin. Alternatively, the depositional environment in Canterbury may result in elevated As in coastal wells as sediments are eroded upstream, carried rapidly downstream and deposited with exposed mineral surfaces from which As is desorbed under reducing conditions. The rapid build-up and burial of sediments containing organic carbon can cause reducing conditions because decomposition of organic matter uses up the available O_2, NO_3 and SO_4 (Smedley & Kinniburgh, 2002). This occurs particularly in wide river valleys where the river carries a high load of sediments (Smedley & Kinniburgh, 2002). The Canterbury Plains largely consist of braided river beds which fit this description. A study by Horton et al (2001) reported arsenopyrite inside mineral veins in the upper Wilberforce valley adjacent to Canterbury. If these mineral veins were exposed, eroded and deposited rapidly downstream it could result in a similar depositional environment to a region of China where As concentrations in groundwater are elevated (Han et al., 2013).

A third option is that there is a layer of peat and organic matter in the sediments near the coast which creates reducing conditions and results in the release of As contained within, or

sorbed to, minerals and the peat material. A study carried out on aquifers in the Venetian Plain in Italy found a correlation between organic matter arising from peat layers in the sediment and the concentration of As (Carraro et al., 2015). It was considered that decomposition of the organic matter caused reducing conditions which induced release of As via the reductive dissolution of iron oxyhydroxides (Carraro et al., 2015).

3.5 Depth Analysis

The concentrations of As in wells of different depths were compared using t-tests. Where a result was less than the detection limit, the value of half the detection limit (DL = 0.02 mg/L) was used for the purposes of this analysis. The categories were binary, e.g. arsenic concentration in wells less than 25 metres deep were compared to As concentration in wells greater than 25 metres deep. There was no statistically significant difference in As concentration according to depth (Table 3.4). There was also no significant correlation between As concentration and depth.

Table 3.4: P-values calculated during t-tests to analyse arsenic concentration and depth.

Category 1	Category 2	*P*-value	Significant Difference?
≤25 m	>25 m	0.73	No
≤50 m	>50 m	0.33	No
≤75 m	>75 m	0.15	No
≤100 m	>100 m	0.21	No
≤125 m	>125 m	0.30	No
≤140 m	>140 m	0.11	No

This is inconsistent with research by the Ministry of Health (2002), who found that deeper bores were more likely to contain detectable As than shallower bores. The dataset for their analysis was small. The Ministry of Health's (2002) result was consistent with a study by Smedley et al (2007) in Burkina Faso which found that deeper wells had higher As concentrations. The relationship between depth and As concentration was considered to be caused by longer residence times allowing reactions between groundwater and sediments

to occur to a greater extent (Smedley et al., 2007). In contrast, a study in Bangladesh found that wells deeper than 150-200 metres exceeded the MAV for As less often than shallower wells (Kinniburgh et al., 2003).

Other literature shows that there is no consistent difference expected in the variation of As concentration with depth. A study in West Bengal found that mid-depth wells had higher As concentrations while a study in Taiwan found that shallower and deeper wells had higher As concentrations than mid-range wells (Smedley, 2003). The British Geological Survey and Department for Public Health Engineering (2001) found that 46% of wells less than 150 metres deep had As concentrations above the WHO guideline, whereas only 5% of wells more than 150 metres deep has As concentrations above the WHO guideline (Ahmed et al., 2004). They also found that maximum As concentrations occurred in wells between 20 and 50 metres deep (Ahmed et al., 2004). In the Duero Basin in Spain, concentrations of As were lower in wells 40-160 metres deep in some cases, potentially due to the formation of sulfide minerals containing As under reducing conditions (Giménez-Forcada & Smedley, 2014). This lack of consistency suggests that other factors such as the presence of minerals and organic matter in the sediments may be more important than depth.

3.6 Temporal (Seasonal) Analysis

Paired t-tests were carried out to determine whether there was a statistically significant difference in As concentration between seasons. Seven wells had been tested in winter and summer. There was no significant difference in As concentration between winter and summer tests (*p*-value of 0.14). A paired t-test showed that the As concentrations measured in wells in either winter or autumn were higher than those measured in summer or spring for the same wells (n = 13 wells, *p*-value = 0.026). Recharge occurs in Canterbury primarily in the winter months (June to August) with the highest average rainfalls in July (National Institute for Water and Atmospheric Science, 2013).

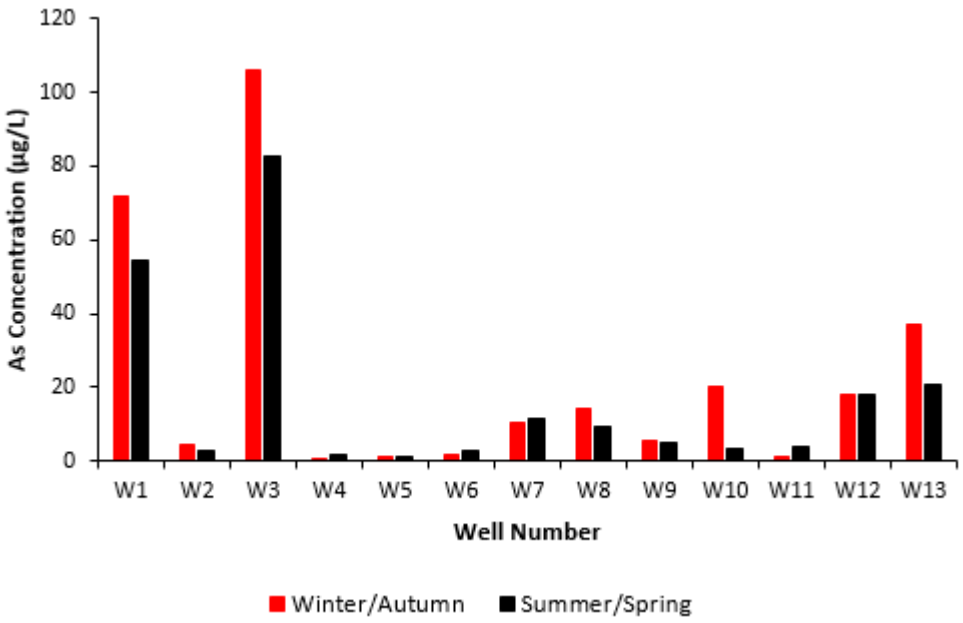


Figure 3.9: Bar chart showing As concentration (µg/L) at 13 wells according to season.

The observed seasonal difference may be due to higher rainfalls causing aquifer recharge in the cooler months and washing sorbed As and other trace metals from the sediments into the groundwater, where they accumulate. This was found to be the case in Anchorage, Alaska, where As concentrations were elevated after recharge events (Munk, 2011). In some areas where superphosphate fertiliser is applied, seasonal variation may also be due to increased infiltration of phosphate into the groundwater from soils during times of high rainfall, taking up sorption sites and increasing the amount of As dissolved in groundwater as opposed to sorbed to the sediments.

A study by Yadav et al (2015) had opposing results, with the concentration of As in groundwater higher in summer than winter. However, summer partially corresponds with monsoon season in Nepal so the same mechanism could be occurring, where As infiltration into groundwater from the sediments is higher due to higher rainfall leading to recharge. Other studies, including a study by Thundiyil et al (2007) in Nevada found no significant difference in As concentration in groundwater depending on season. Frost et al (1993) found that As concentration in wells varied over time in the Snohomish County, Washington, U.S.A; but no particular seasonal trends were identified.

3.7 Soil Type Analysis

The elevated-As wells from the Environment Canterbury database were categorised according to the parameters from Landcare's Fundamental Soil Layer maps (Landcare, 1996).

Soil Type

Wells located within orthic gley soils and fluvial recent soils had the highest concentrations of dissolved As (Figure 3.10A). The single well located in sandy raw soils contained 15-20 µg/L of As. More wells in sandy raw soils should be tested to determine whether most wells within sandy raw soil contain elevated levels of As. Wells located in fluvial recent soils had a wide range of As concentrations with a high variance. Wells located in orthic gley soils had a far smaller range of As concentrations so it is more likely that wells within these soils commonly have elevated As concentrations. Gley soils are typically reducing (Landcare Research, 2016). Reducing conditions can cause the release of As sorbed to sediments under the reductive dissolution mechanism as outlined in Chapter 1.

Cation Exchange Capacity

Wells located in soils with a cation exchange capacity (CEC) of 12 to 24 cmoles(+)/kg had elevated As concentrations that were less variable than wells in soils with higher CEC values (Figure 3.10C). The elevated-As (5 to 20 µg/L) wells were present in soils with this CEC range. The CEC is sometimes related to pH as it can be defined as the number of exchangeable cations per weight of dry soil that can be held, and can be exchanged with water, at a particular pH.

Particle Size

Wells located in soils with silt-sized (0.002 mm < x <0.063 mm) particles had the highest median As concentration (Figure 3.10D). This was consistent with previous research which found that aquifers in West Bengal and Bangladesh with elevated As concentrations generally existed in soils with sands, silts and clays (Smedley & Kinniburgh, 2002). Silt-sized

soils are typically small which may mean that groundwaters contained within them are less oxic because there are less spaces through which oxygen can be introduced.

Soil Macroporosity and Drainage

There was no consistent trend between soil macroporosity and dissolved arsenic concentration. Shallow-depth wells surrounded by high macroporosity soils had elevated concentrations of As (Figure 3.10F). This was unexpected as wells located in high macroporosity soils should be more oxic, and previous studies have shown that DO concentration tends to be negatively correlated with As (Ahmed et al., 2004). Macroporosity is related to soil drainage in that soils with greater macroporosity are likely to have better soil drainage. Wells in moderately well-drained soils had the highest concentrations of dissolved As, and wells found in poorly-drained soils contained the lowest concentrations of As (Figure 3.11F). The reason for this is unknown.

Flood Return Interval

Wells with As concentrations higher than 1 µg/L were present in areas with a slight flood return interval of less than 1 flood in 60 years (Figure 3.10H). This may be because these wells were located in lower lying areas where chemicals tended to accumulate. Ahmed et al (2004) found that wells within the flood plains of the Bengal Basin were moderately to severely enriched with As. They also found that wells in depressed land characterised by numerous lakes and swamps were moderately enriched with As (Ahmed et al., 2004). Smedley et al (2003) found elevated As concentrations in the low-lying areas of the Huhhot Basin in Inner Mongolia. The elevated As in these low-lying areas corresponded with elevated dissolved organic carbon (DOC) concentrations (Smedley et al., 2003).

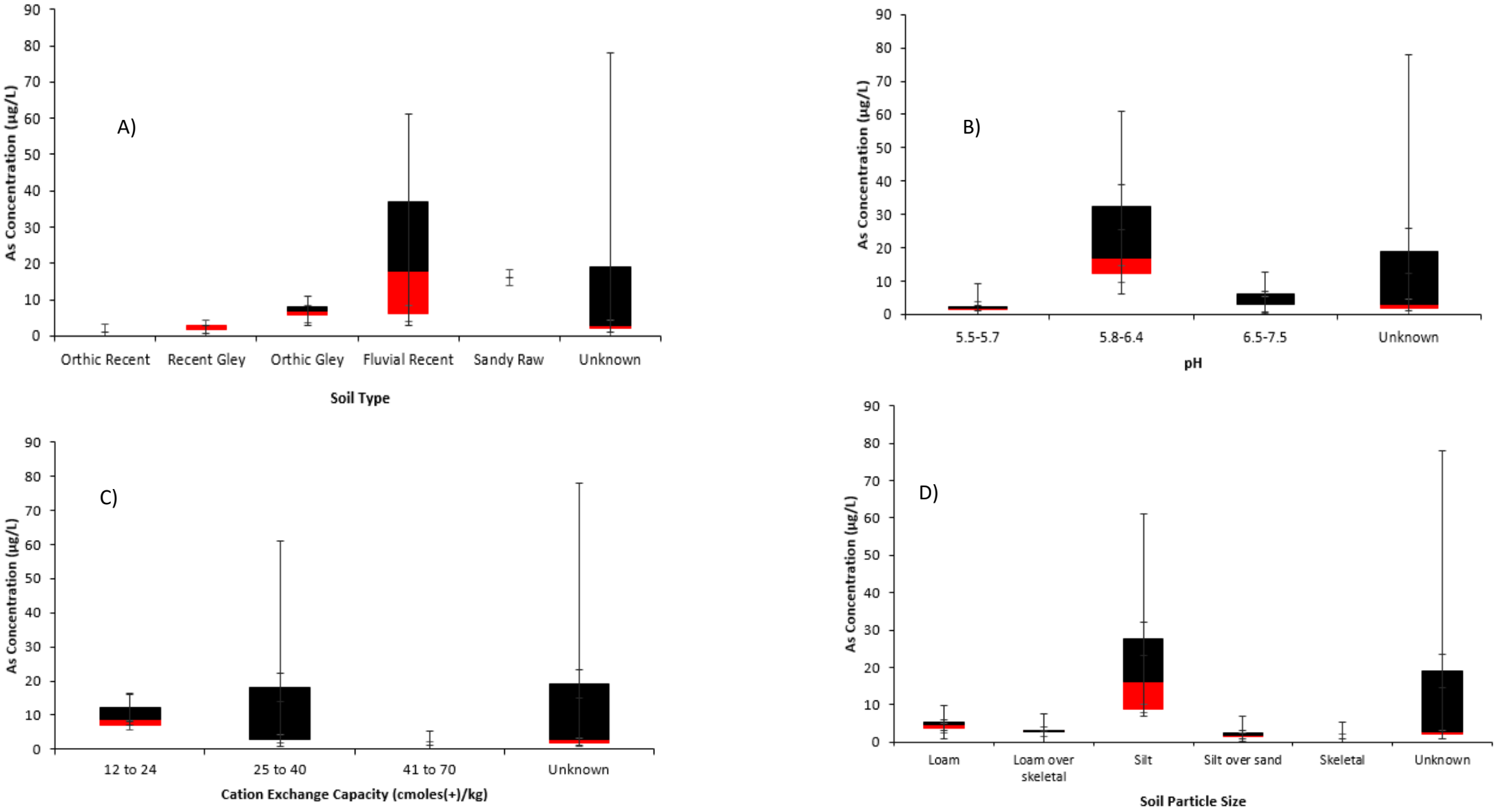


Figure 3.10 A - E: Arsenic concentration in groundwater according to different soil characteristics including soil type (A), pH (B), cation exchange capacity (C) and soil particle size (D).

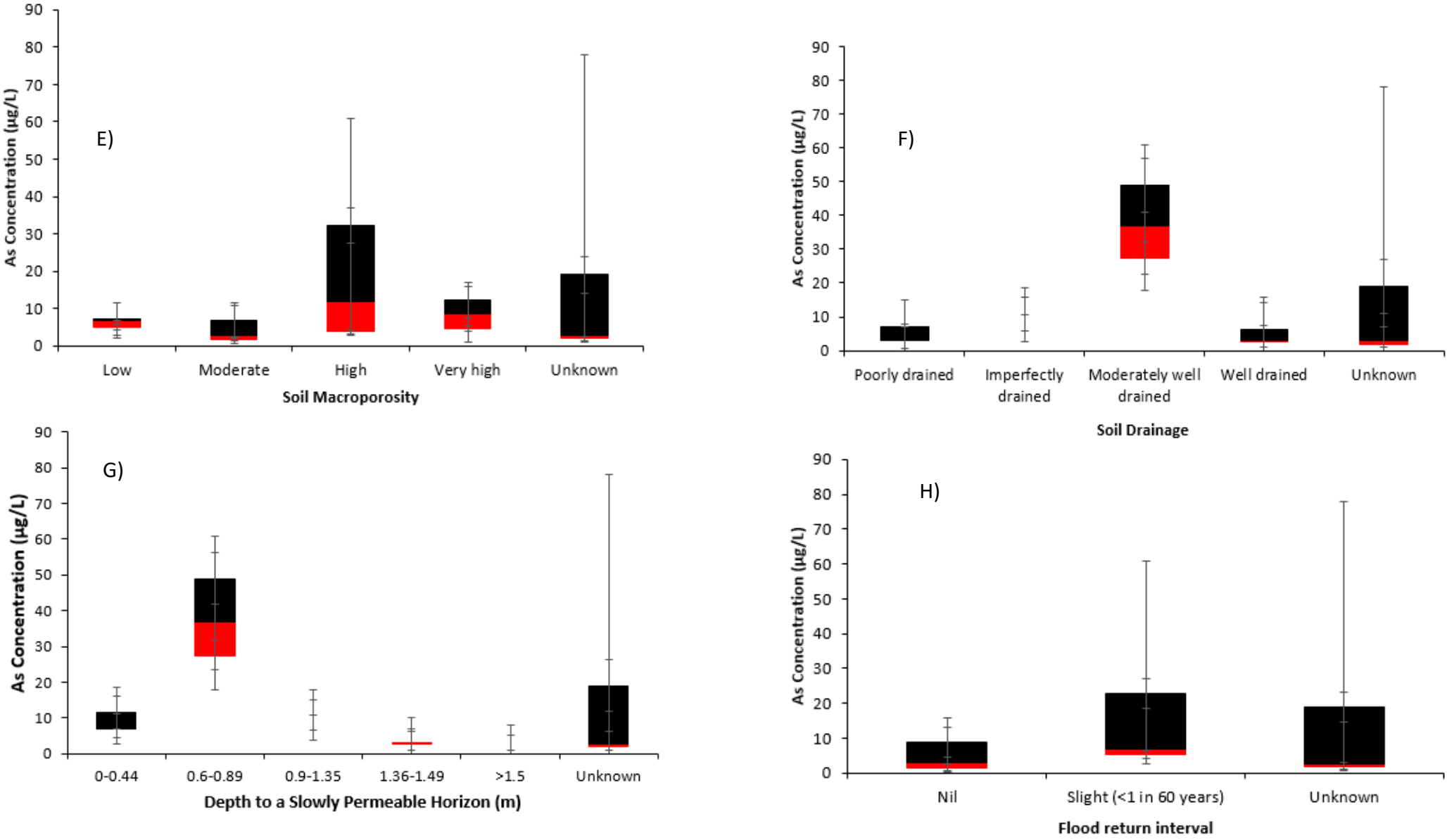


Figure 3.10 F - I: Arsenic concentration in groundwater depending on soil macroporosity (E), soil drainage (F), depth to a slowly permeable horizon (G) and flood return interval (H) (n = 19) (Landcare Research, 1996).

Depth to a Slowly Permeable Horizon

Depth to a slowly permeable horizon is defined as the depth at which soils have a permeability of less than 44 mm/hour (Landcare Research, 2006). Wells located in soils with 0.6 to 0.89 metres to a slowly permeable horizon had elevated concentrations of As compared to wells in soils with other depth ranges (Figure 3.10G). Wells in soils with up to 0.44 metres to a slowly permeable horizon had slightly elevated As concentrations. Smedley (2003) suggested that having less permeable strata (for example, those with a lesser depth to a slowly permeable horizon) may cause groundwater to flow more slowly. Generally slow flowing groundwater is more likely to have elevated As concentrations (Smedley, 2003).

Soil pH

Wells located in soils with pH 5.8 to 6.4 had As concentrations ranging from 5 to 61 µg/L, with a high median of 17 µg/L (Figure 3.10B). The lowest concentration in this range, 5 µg/L, is elevated compared to the As concentration in wells located in soils with other pH ranges. Though not a statistical test, this may indicate that there is an actual difference in As concentration in groundwater depending on soil pH. Wells located in soils with a pH range of 6.5 to 7.5 had lower concentrations of dissolved As (ranging from 0 to 15 µg/L).

3.8 Summary and Interpretation of Results

The results from Chapter 3 indicated that there were significant correlations between As, Fe and Mn, and a significant relationship between As concentration and dissolved organic carbon concentration, but no relationship between As concentration and depth. Several studies have concluded that significant correlations between As and Fe and Mn could indicate that the reductive dissolution of Fe oxides is responsible for releasing As into groundwater. There was a moderately strong linear relationship between As concentration and the concentration of dissolved phosphorus species in Canterbury groundwater, and a mutually exclusive relationship between As and both DO and SO_4. Elevated As concentrations may tend to occur in anoxic environments with reducing conditions. In addition, there may be a difference in As concentration in wells depending on the time of year and proximity to the coast.

Chapter 4

Results and Discussion: Sampling Data Analysis

Chapter 4 aims to further investigate the mechanism of arsenic (As) release into Canterbury groundwater by analysing the composition of Canterbury groundwater from samples collected during the sampling phase of this research. The relationship between As concentration, soil characteristics and environmental conditions will be investigated. The hypotheses arising from the analysis of Environment Canterbury data are as follows:

1. Arsenic concentration is positively related to Fe, Mn, and dissolved reactive phosphorus (DRP) concentrations and inversely related to dissolved oxygen (DO) concentrations.
2. Wells nearer to the coast are more likely to have elevated As than inland wells.
3. The concentration of As in groundwater is higher in cooler months than warmer months.

To investigate the three hypotheses, eighteen wells across the Canterbury region were sampled twice: once in autumn and once in winter. The parameters measured were As, conductivity, pH, DO, temperature, turbidity, sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl), sulfate (SO_4), DRP, total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), NO_3, Fe, Mn, calcium (Ca), copper (Cu), zinc (Zn), lead (Pb), vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), cadmium (Cd), and antimony (Sb).

4.1 Water Quality

4.1.1 General Water Chemistry, Nutrients and Carbon

Physicochemical Variables

Wells were paired; wells labelled “A” being As-elevated wells, and “C” being low-As wells. The pH ranged from 6.5 to 8.6. The concentration of DO ranged from 0.04 mg/L to 8.71 mg/L and wells 8A and 8C had low DO concentrations. The DO concentration was much higher in July than April for well 2A. The reason for this is unknown. The temperature

ranged from 7.3°C to 19.0°. Well 9A, which had a temperature in July of 19°C, was the only well at which any UV treatment was undertaken prior to sample collection. The temperature was significantly lower in July than April (*p*-value of 0.021). This is most likely due to the change in season. The conductivity ranged from 95.1 µS/cm to 1030 µS/cm and well 8A had the highest conductivity which may be due to some saline intrusion as the well was located within 800 metres of a saltwater body. Turbidity was only measured during the second round of sampling and ranged from below the detection limit to 24 NTU. Wells 7A and 7C both had low turbidity values which may be attributed to a particular geographical or geological influence because these wells were located near each other. Two different wells, no more than 8 metres from each other and with the same depth to within one metre, were used to collect samples for '6C' because one well had been shut down during the July round of sampling and was unable to be restarted. Samples were collected from the neighbouring well, '6Cb' instead.

Table 4.1: Results for general water quality parameters. Two wells located approximately 5-10 metres from each other were used for low-As well 6 as access to well 6C was not available in July. NT = not tested.

Well	pH		DO (mg/L)		Temperature (°C)		Conductivity (µS/cm)		Turbidity (NTU)	
	April	July	April	July	April	July	April	July	April	July
1A	6.8	7.5	2.23	1.81	13.0	12.2	341	339	NT	14.9
1C	6.6	7.2	NT	8.70	18.2	12.2	NT	210	NT	<0.01
2A	7.4	8.0	0.73	8.71	14.5	14.0	672	679	NT	0.62
2C	7.9	7.5	4.98	1.86	13.9	13.9	758	824	NT	0.09
3A	6.5	7.0	3.52	6.76	13.2	12.0	NT	95	NT	1.80
3C	6.6	7.3	6.85	6.67	13.4	8.8	NT	140	NT	0.27
4A	6.8	7.5	0.11	1.77	12.8	12.2	NT	240	NT	0.45
4C	7.5	6.8	6.66	5.84	12.5	13.3	NT	233	NT	0.25
5A	6.8	7.0	4.53	6.12	14.0	7.3	127	119	NT	0.59
5C	6.5	6.7	4.00	5.93	13.4	14.0	99	99	NT	0.37
6A	7.2	7.0	0.14	0.07	14.0	13.8	136	132	NT	0.57
6C/6Cb	7.8	7.6	6.34	5.65	13.7	14.5	100	114	NT	0.02
7A	7.0	6.6	4.18	0.90	13.3	13.1	358	393	NT	0.05
7C	7.5	7.1	3.30	3.12	14.5	14.4	118	118	NT	0.03
8A	7.1	6.9	0.70	0.04	14.3	14.2	1029	1030	NT	4.27
8C	7.4	7.0	0.65	0.36	13.3	13.4	132	131	NT	5.11
9A	7.8	8.6	3.98	3.46	19.0	16.5	246	192	NT	24.0
9C	6.9	7.4	3.25	5.37	14.9	10.2	206	183	NT	0.86

Major Ions

The concentrations of Na ranged from 4.26 mg/L to 159 mg/L (Table 4.2). The concentrations of K ranged from 0.801 mg/L to 14.2 mg/L and Ca concentrations ranged from 7.55 mg/L to 81.7 mg/L. Magnesium concentrations ranged from 1.28 mg/L to 45.2 mg/L and the concentrations of Cl ranged from 2.19 mg/L to 188 mg/L. The concentrations of SO_4 ranged from lower than the detection limit in a Kaikoura well to 65.5 mg/L in a Southeast Christchurch well. The low concentration of SO_4 in Kaikoura was not consistent with the analysis of Environment Canterbury data, which showed elevated concentrations of >5 mg/L SO_4 although it should be noted that this was for a different well. HCO_3 was not measured directly, but was calculated based on an inorganic carbon analysis. The concentrations of HCO_3 ranged from 19.9 mg/L to 259 mg/L. Wells 2A, 2C, and 8A (and to a certain extent 7A) had elevated major ion concentrations and conductivity values and were in close proximity to the coast (<4.5 km). It is suggested that the elevated ion concentrations and conductivities may be due to saline intrusion into the aquifer.

Nutrients

Considerable variation in DRP, TC, TIC, TOC, and NO_3 concentrations was noted (Table 4.3). The concentration of DRP ranged from 0.092 mg/L at well 1C in Kaikoura to >1.1 mg/L at well 1A in Kaikoura. The concentrations of DRP measured at well 1A were determined to be 1.14 mg/L and 1.21 mg/L. The mixed results at Kaikoura were consistent with the map produced on ArcGIS in Chapter 3 (Figure 3.4), which showed both low and high DRP concentrations at Kaikoura. The concentration of NO_3 ranged from below the detection limit to 33.7 mg/L. This higher concentration was far outside the realms of what was measured at the other wells, but given that both rounds of sampling resulted in NO_3 concentrations higher than 30 mg/L at that well, it is considered to be accurate.

Carbon

The concentration of total carbon (TC) ranged from 5.71 mg/L to 53.9 mg/L and the concentration of total inorganic carbon (TIC) ranged from 10.4 mg/L to 51.0 mg/L. Total organic carbon concentration (TOC) ranged from below the detection limit to 11.6 mg/L.

Table 4.2: Concentrations of dissolved major ions in groundwater (mg/L). Well 6Cb, approximately 5 metres from 6C, was used in July as 6C was not available. NT = not tested.

Well	Na		K		Ca		Mg		Cl		SO_4		HCO_3	
	April	July	April	July	April	July	April	July	April	July	April	July	April	July
1A	25.2	26.1	1.05	1.12	33.7	37.1	8.59	9.17	4.57	4.50	<0.015	0.0899	238	252
1C	6.98	8.07	1.23	1.40	26.6	31.3	4.17	4.93	4.82	3.96	13.6	14.1	NT	120
2A	92.1	89.6	2.31	2.30	56.0	56.9	9.51	9.81	110	110	9.10	9.01	200	218
2C	93.4	106	2.73	3.11	69.7	81.7	11.1	12.7	142	144	15.2	24.5	231	259
3A	5.03	6.41	0.991	1.31	9.46	12.4	1.28	2.34	3.70	3.40	4.02	4.35	19.9	56.3
3C	7.67	9.66	1.31	1.64	12.3	16.0	3.29	4.12	4.16	4.35	1.93	3.22	70.5	89.8
4A	17.9	21.6	1.25	1.47	23.0	27.5	6.07	7.44	8.92	9.20	1.88	1.78	74.1	155
4C	18.4	30.2	1.73	2.02	17.8	21.0	6.61	7.79	12.9	12.6	15.9	16.7	121	109
5A	5.91	7.04	1.67	1.92	15.9	18.0	2.05	2.21	4.47	3.23	4.01	3.98	68.1	85.6
5C	4.26	5.01	0.920	1.09	12.8	14.9	1.43	1.63	2.54	2.19	4.65	5.19	74.8	67.0
6A	11.1	13.6	1.19	1.45	11.7	14.4	2.61	3.14	6.35	6.23	0.705	0.630	96.1	79.6
6C/6Cb	7.91	9.66	0.801	0.967	10.2	13.9	1.86	2.37	3.18	4.67	3.27	3.22	52.9	64.6
7A	29.8	36.7	3.46	4.16	31.5	38.0	6.32	7.74	45.5	46.2	<0.015	0.0738	160	188
7C	8.75	10.6	1.01	1.05	11.9	13.8	2.28	2.71	4.54	4.45	2.82	3.27	69.6	69.6
8A	131	159	12.0	14.2	28.8	34.2	38.4	45.2	185	188	64.2	65.5	201	231
8C	12.1	14.7	1.50	1.78	7.55	9.05	5.14	6.26	5.44	7.55	0.428	0.801	130	85.4
9A	21.5	25.6	1.47	1.79	14.8	16.4	4.81	5.54	24.2	18.7	6.00	5.36	75.5	86.0
9C	10.8	13.0	1.20	1.42	21.9	24.9	3.29	3.89	8.21	7.78	11.7	9.97	95.7	99.2

Table 4.3: Concentrations of nutrients dissolved in groundwater (mg/L). Well 6Cb, which was approximately 5 metres from 6C, was used in July as 6C was not pumping. NT = Not tested.

Well	DRP		TC		TIC		TOC		NO_3	
	April	July	April	July	April	July	April	July	April	July
1A	>1.1	>1.1	53.9	50.1	46.8	49.5	7.08	0.59	<0.05	<0.05
1C	0.098	0.092	NT	22.2	NT	23.6	NT	<0.05	4.10	2.91
2A	0.11	0.11	36.3	42.3	39.4	42.9	<0.05	<0.05	<0.05	<0.05
2C	0.11	0.11	48.7	49.4	45.6	51.0	3.18	<0.05	0.57	0.46
3A	0.094	0.096	4.30	11.6	3.93	11.0	0.36	0.59	1.37	1.23
3C	0.099	0.10	12.4	18.6	13.8	17.6	<0.05	0.95	<0.05	<0.05
4A	1.07	0.40	26.2	31.2	14.5	30.5	11.6	0.68	<0.05	<0.05
4C	0.097	0.098	33.0	20.6	23.8	21.5	<0.05	<0.05	31.6	33.7
5A	0.096	0.094	12.8	18.4	13.4	16.8	<0.05	1.60	0.67	0.70
5C	0.095	0.095	18.5	14.4	14.7	13.1	3.80	1.28	1.06	1.23
6A	0.12	0.13	30.2	16.9	18.9	15.6	9.46	1.31	<0.05	<0.05
6C/6Cb	0.10	0.098	19.8	13.9	10.4	12.7	4.92	1.24	0.43	0.62
7A	0.55	0.45	27.3	43.3	31.5	37.1	<0.05	6.19	<0.05	<0.05
7C	0.10	0.10	5.71	11.0	13.7	13.7	1.54	<0.05	0.47	0.49
8A	0.17	0.12	39.3	39.3	39.6	45.5	<0.05	<0.05	3.53	3.48
8C	0.11	0.10	25.7	20.4	25.7	16.8	<0.05	3.60	<0.05	<0.05
9A	0.10	0.10	12.7	20.6	14.8	16.9	<0.05	3.74	0.70	0.69
9C	0.094	0.094	16.0	13.4	18.8	19.5	<0.05	<0.05	9.48	7.46

4.1.2 Arsenic

Arsenic (As) was detected in all 18 wells (Table 4.4) at concentrations up to 111 µg/L. Both filtered and unfiltered samples were collected, allowing the dissolved and total concentrations of As to be determined. Most As was present in the dissolved phase rather than the solid particulate phase. The six sites with the highest As concentrations were, in order from highest detectable As to lowest detectable As: 7A, 1A, 4A, 6A, 9A and 8A. Elevated As concentrations were observed at wells 1A, 4A and 7A (Figure 4.1) which had significantly higher As concentrations than other sites. These sites were located in Christchurch, Ohoka and Kaikoura so were not near each other spatially.

Table 4.4: Arsenic concentrations in paired groundwater wells (μg/L). Well 6Cb was sampled in July instead of well 6C which was not available.

Well	Dissolved As (April)	Dissolved As (July)	Total As (April)	Total As (July)
1A	69.1	72.3	71.1	76.1
1C	<0.1	0.111	<0.1	0.116
2A	<0.1	0.260	<0.1	0.248
2C	<0.1	0.262	<0.1	0.276
3A	<0.1	0.104	<0.1	0.107
3C	<0.1	0.192	<0.1	0.146
4A	15.6	17.1	15.8	17.5
4C	<0.1	0.102	<0.1	<0.1
5A	<0.1	<0.1	0.122	0.383
5C	<0.1	0.134	<0.1	0.142
6A	3.71	4.69	3.71	4.63
6C/6Cb	0.930	0.971	0.887	0.988
7A	100	111	101	110
7C	1.06	1.13	0.936	1.13
8A	0.741	1.06	0.619	1.28
8C	0.581	0.748	0.388	0.708
9A	1.08	1.42	1.09	1.39
9C	0.126	0.236	0.130	0.228

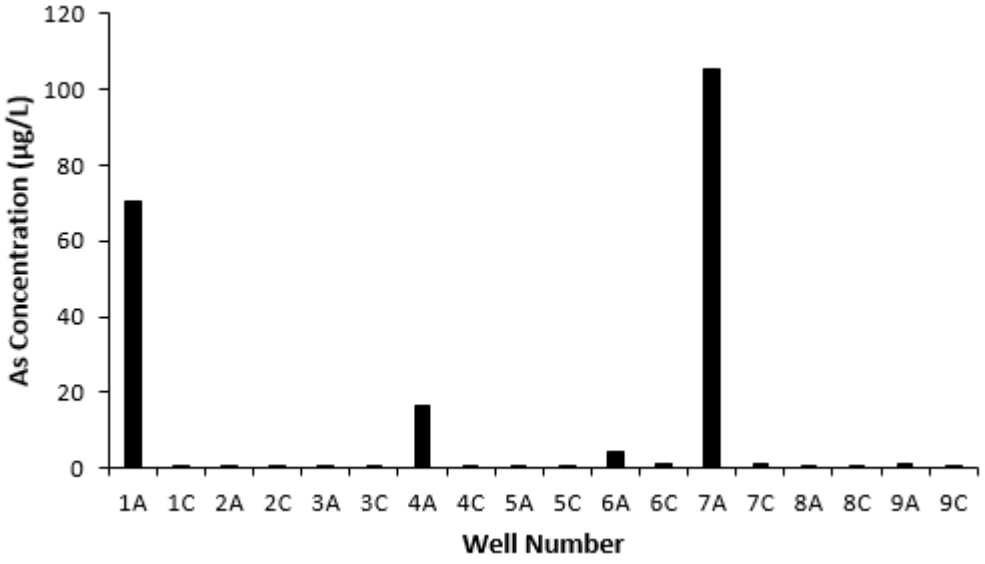


Figure 4.1: Concentration of dissolved As at each site (µg/L).

Of the wells samples, 16.7% exceeded the drinking water standard of 10 µg/L. It should be taken into account that the wells selected for this study were not random. Another study that focussed on the Saltwater Creek-Wooded-Waikuku area found that 19 of the 121 wells sampled exceeded the drinking water MAV (maximum allowable value) for As, with a maximum recorded concentration of 170 µg/L (Pattle Delamore Partners Ltd, 2001). In an analysis of 45 coastal wells around New Zealand (but primarily outside of Canterbury), the Ministry of Health (2002) found that no wells exceeded the drinking water standard. In the Waikato region, a study found that one in ten samples exceeded the MAV As in drinking water and the highest measured As concentration was 888.5 µg/L (Environment Waikato, 2006). The elevated-As wells were centred in three locations and only 3% of wells outside of these locations had As concentrations that exceeded the MAV (Environment Waikato, 2006). Arsenic concentrations in groundwater in Bangladesh and West Bengal, where the dominant mechanism of As-release into groundwater is the reductive dissolution of Fe and Mn minerals, range from 0.5 to 3200 µg/L (Smedley & Kinniburgh, 2002). The concentration of As in Taiwanese groundwater ranges from 10 to 1800 µg/L with a mean of 500 µg/L which is 50 times greater than the New Zealand MAV for drinking water (Smedley & Kinniburgh, 2002).

4.1.3 Other Trace Elements

The concentrations of Mn ranged from 0.151 µg/L to 1140 µg/L (Table 4.5). The concentrations of Fe ranged from 10.9 µg/L to 3460 µg/L. Copper concentrations ranged from below the detection limit to 27.7 µg/L and the concentrations of Zn ranged from below the detection limit to 140 µg/L. Copper was elevated in well 8A. Elevated Zn was found in coastal Christchurch wells. Lead concentrations ranged from below the detection limit to 3.01 µg/L and were significantly higher in July than April (p<0.05). High Pb concentrations were found in the Kaikoura wells, Northeast Christchurch wells, and coastal Christchurch wells. There was variation in results between sampling rounds. Well 6C and 7C both had much higher Zn concentrations in April than July. At well 5A the concentration of Cu was much higher in July than April. In July the Fe concentration at well 3C was almost doubled and the concentration of Mn was more than doubled, compared to April.

Table 4.5: Dissolved trace element concentrations in paired wells (µg/L). Well 6C was not sampled in July as it was not pumping. Instead the nearby, similar well 6Cb was used.

Well	Mn		Fe		Cu		Zn		Pb	
	April	July	April	July	April	July	April	July	April	July
1A	541	585	1900	1900	<1.0	1.66	21.3	35.9	<0.1	1.23
1C	0.284	0.151	37.7	22.8	4.00	4.56	16.1	7.25	0.364	1.53
2A	4.69	5.40	263	316	<1.0	<1.0	4.82	<10.0	<0.1	0.168
2C	16.8	15.8	845	739	<1.0	1.14	23.1	20.6	<0.1	0.869
3A	6.37	5.47	96.8	125	1.69	<1.0	18.3	<10.0	0.142	0.817
3C	6.14	13.8	774	1490	<1.0	<1.0	<10.0	<10.0	<0.1	0.238
4A	269	332	1460	1840	<1.0	<1.0	16.0	<10.0	<0.1	0.417
4C	0.174	0.246	20.9	18.5	<1.0	1.91	11.0	<10.0	0.115	0.806
5A	2.46	2.20	68.1	71.6	4.24	27.7	21.9	16.2	0.309	3.01
5C	0.159	0.169	20.2	20.6	2.04	4.83	36.4	33.5	0.972	2.39
6A	48.2	59.1	112	166	<1.0	<1.0	<10.0	<10.0	<0.1	0.215
6C	0.471	<0.1	10.9	11.9	1.93	<1.0	140	<10.0	0.171	<0.1
7A	659	776	2900	3460	<1.0	2.59	61.2	79.8	<0.1	1.63
7C	2.24	2.53	28.2	21.4	2.08	1.61	52.1	6.87	0.229	1.11
8A	952	1140	105	173	13.2	15.0	18.8	27.5	<0.1	0.605
8C	99.0	119	63.5	80.3	1.74	1.84	27.7	<10.0	<0.1	0.887
9A	0.826	0.459	30.2	15.4	<1.0	<1.0	24.2	<10.0	0.106	0.114
9C	1.11	1.79	20.3	24.2	5.35	3.47	39.6	46.4	0.237	0.224

Wells 1A, 4A, 6A and 7A were the only ones with concentrations of Mn, Fe and As higher than 1 µg/L (Figure 4.2).

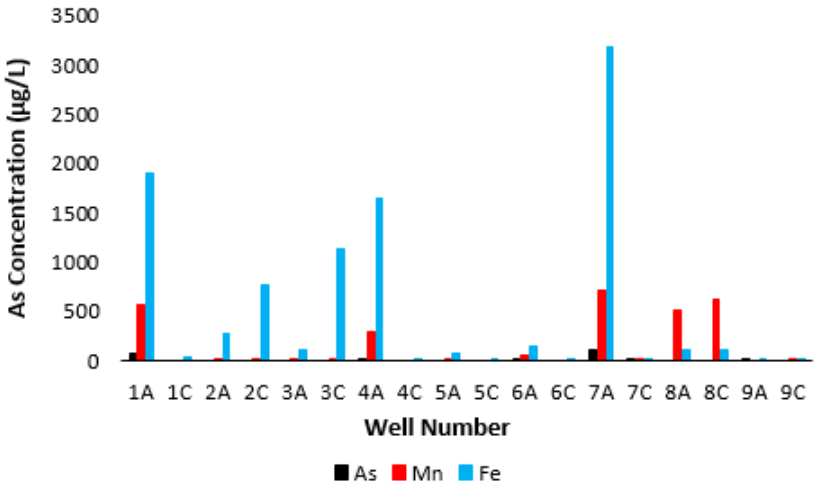


Figure 4.2: Concentration of dissolved As, Mn and Fe at each site (µg/L).

4.2 Comparison to Drinking Water Standards

Several parameters exceeded the drinking water standards or were outside of the acceptable range. The standards for aluminium (Al), As, Fe, Mn, pH, and turbidity were breached in some wells (Table 4.6).

Table 4.6: Comparison of sampling results to drinking water standards. NT = not tested.

Parameter	DWS	Maximum/minimum measured value	Number of wells not meeting DWS (Round 1)	Number of wells not meeting DWS (Round 2)
Aluminium	0.1	<0.001 – 0.181	0	1
Arsenic	0.01	<0.0001 – 0.111	3	3
Iron	0.2	0.0109 – 3.46	6	6
Manganese	0.4	0.00015 – 1.14	3	3
pH	7.0 – 8.5	6.5 – 8.6	8	5
Turbidity	2.5	<0.01 – 24	NT	4

4.3 Comparison to LLUR Database

The location of each well was checked using Environment Canterbury's Listed Land Use Register to find out whether any activities listed under the HAIL (Hazard Activities and Industries List) occurred at the site (Table 4.6). This is so it could be determined whether there was any contaminated land that could be a source of As because of historical use or storage of particular compounds. Of the wells with associated HAIL sites, the only one with an elevated As concentration was well 6A. This may be due to the storage of persistent pesticides on-site. The pesticide lead arsenate was used from the early 1900s through until the late 1960s (Gaw et al., 2006).

Table 4.7: Activities listed on the listed land use register associated with sampling sites.

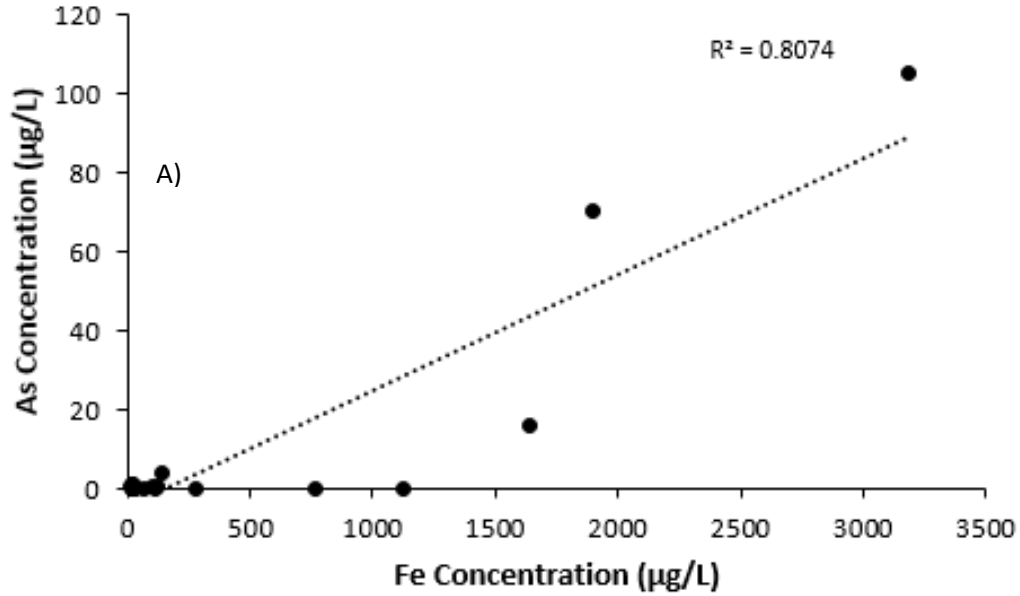
Well	LLUR Site	Well	LLUR Site
1A	No associated sites	1C	No associated sites
2A	No associated sites	2C	No associated sites
3A	No associated sites	3C	Landfill associated with this site.
4A	No associated sites	4C	No associated sites
5A	Storage of tanks or drums for fuel, chemicals, or liquid waste associated with this site	5C	No associated sites
6A	Storage of tanks or drums for fuel, chemicals, or liquid waste associated with this site. Persistent pesticide bulk storage or use is also associated with this site.	6C	No associated sites
7A	No associated sites	7C	No associated sites
8A	No associated sites	8C	No associated sites
9A	Storage of tanks or drums for fuel, chemicals, or liquid waste associated with this site	9C	Persistent pesticide bulk storage or use is associated with this site.

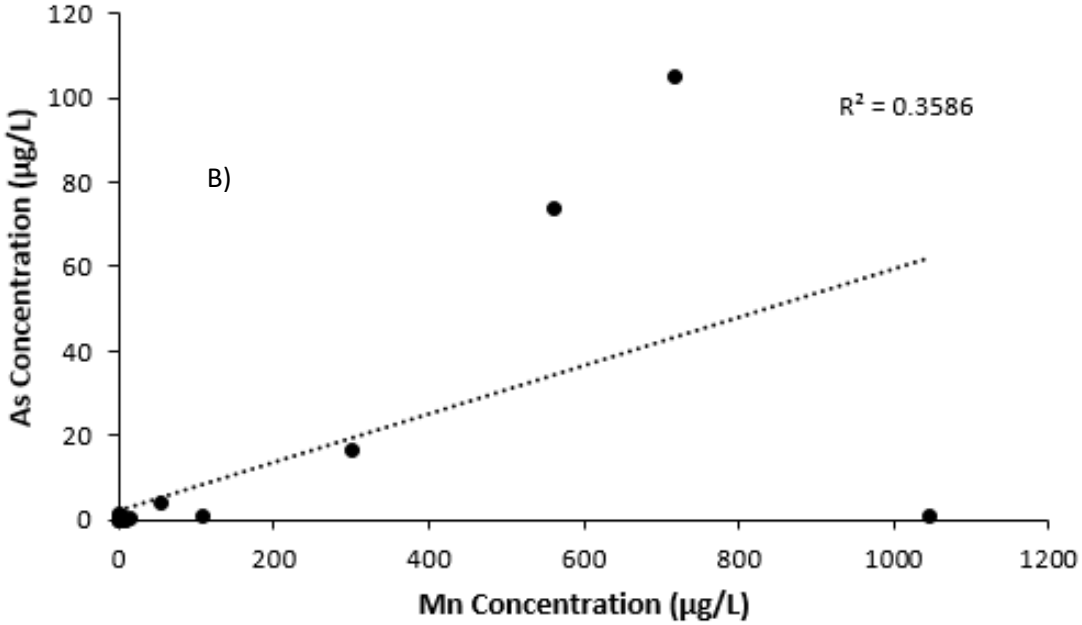
4.4 Comparison of 'A' and 'C' Wells

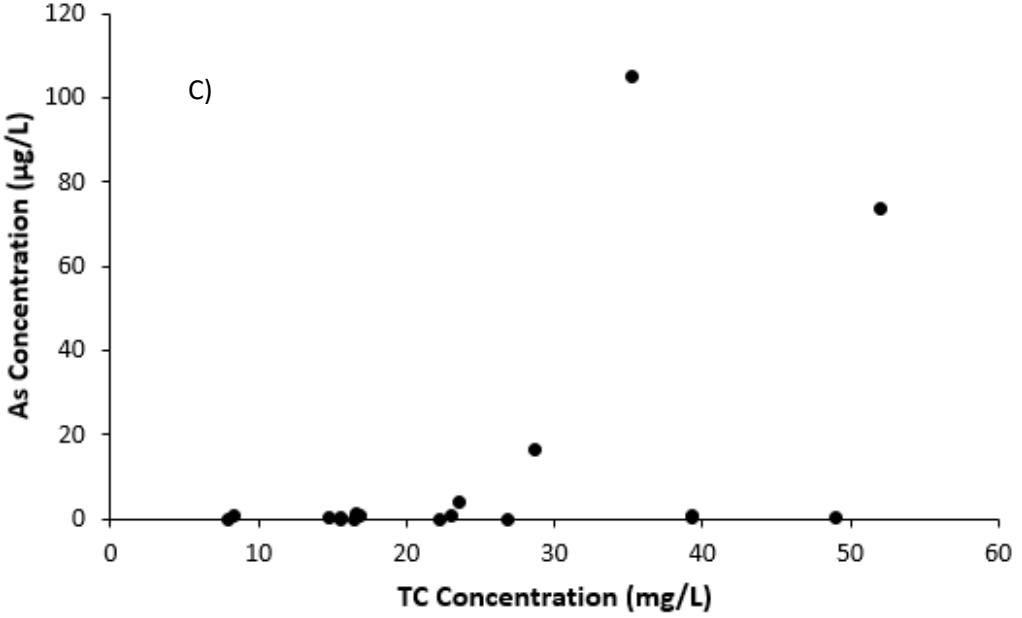
There was no significant difference in As concentration between 'A' wells and 'C' wells (p>0.05). There was also no significant difference in the concentration of any trace elements, or the values of physicochemical parameters in 'A' wells compared to 'C' wells, with the exception of Mn which was elevated in 'A' wells.

4.5 Relationship between Arsenic and Physicochemical Parameters

Scatter graphs were plotted to determine whether there was a correlation between the concentration of As and other parameters.







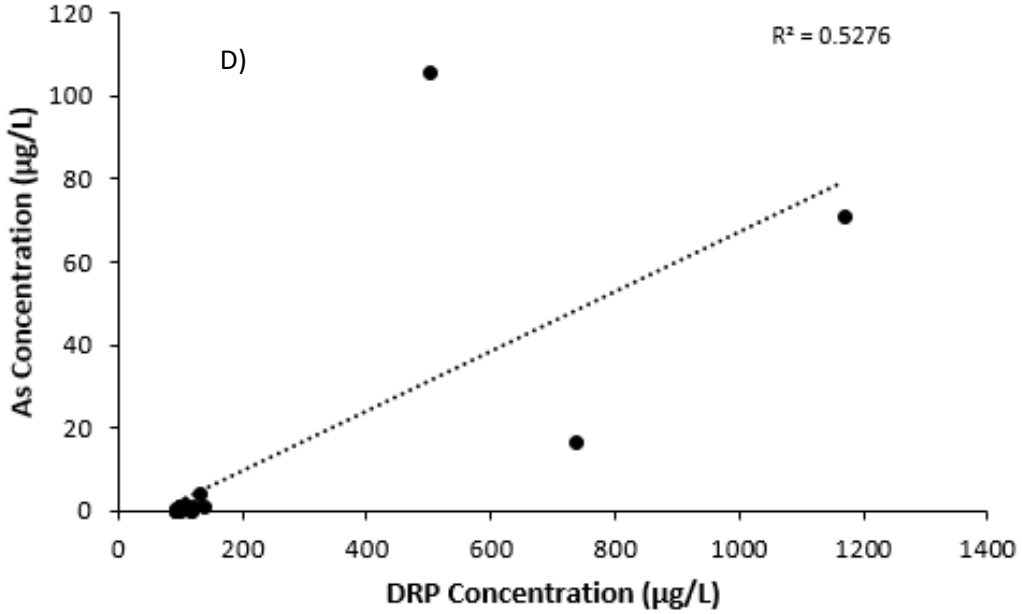
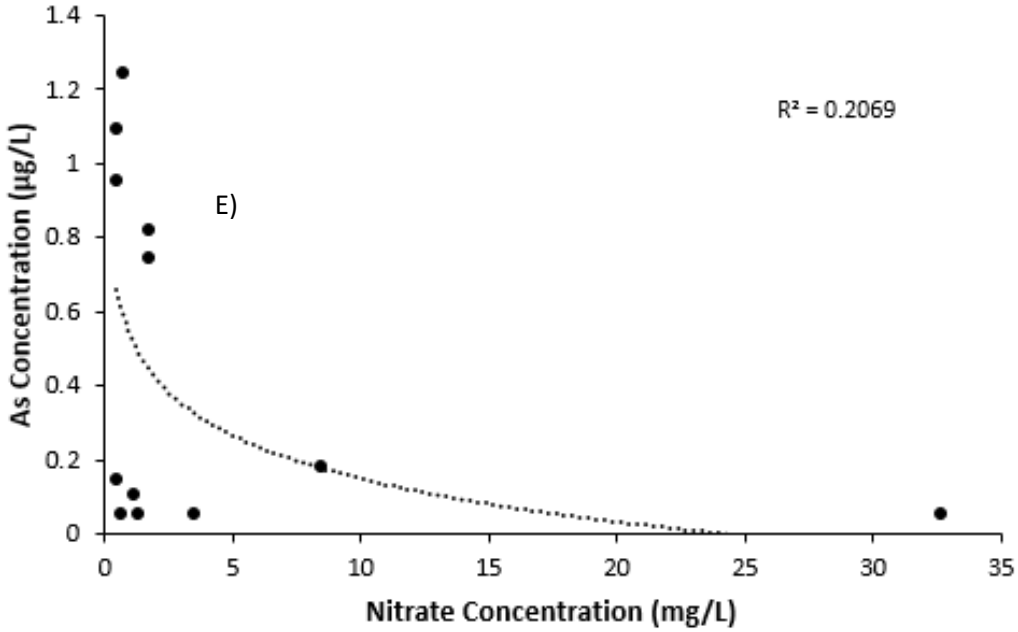
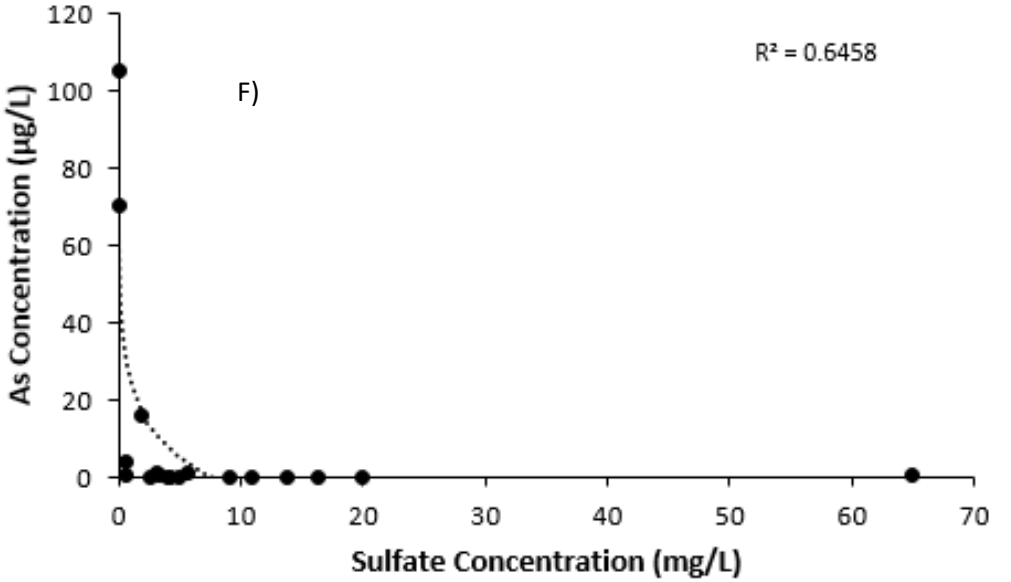
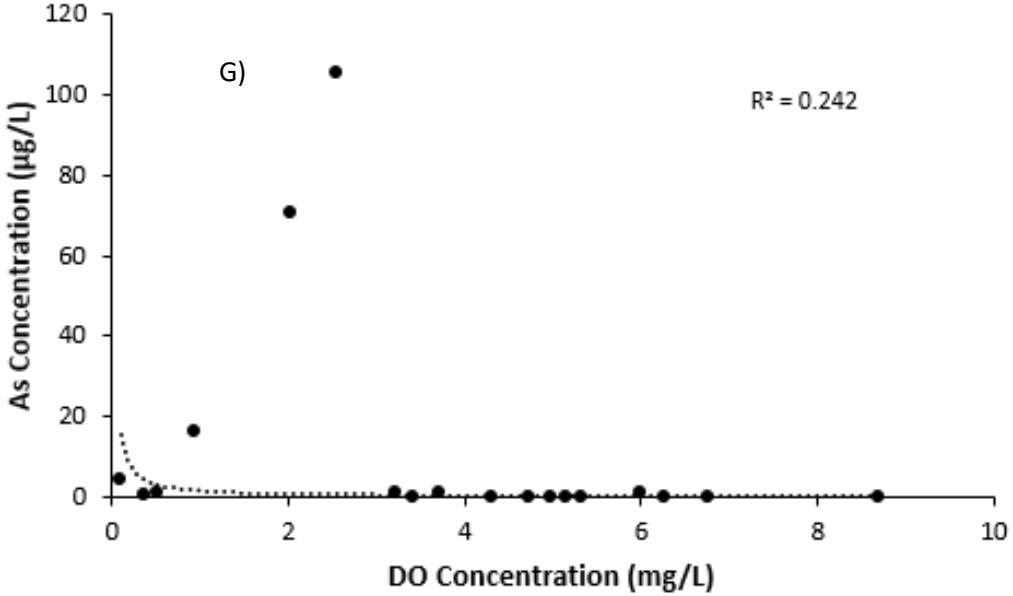


Figure 4.3 A – D: Correlation of dissolved As with Fe (A), Mn (B), TC (C) and DRP (D).







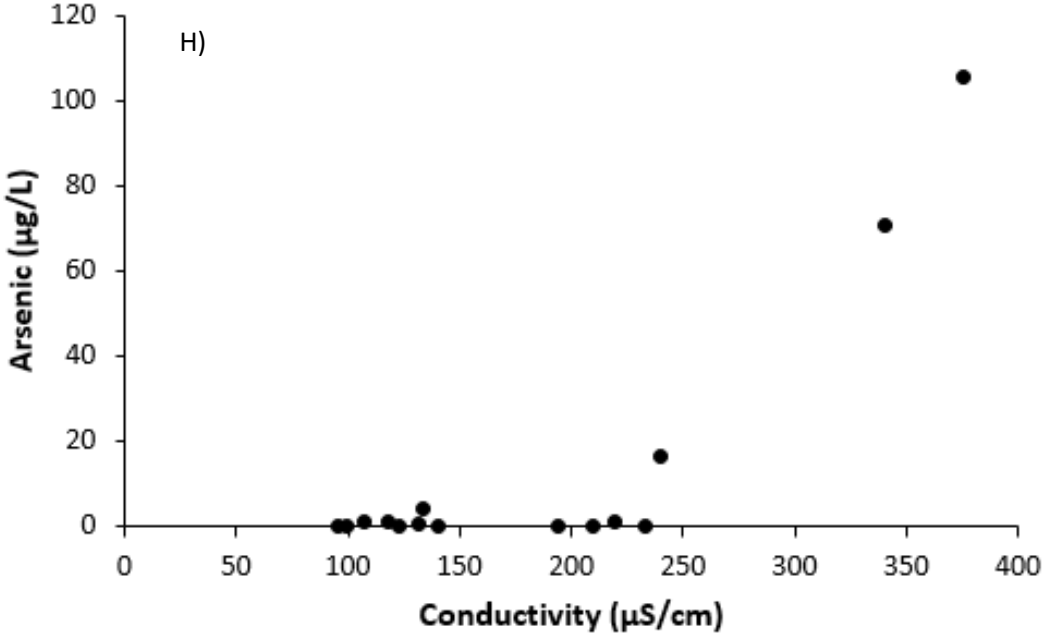


Figure 4.3 E - H: Correlation between dissolved As and NO_3 (E), SO_4 (F), DO (G) and conductivity (H).

Iron and Manganese

The dissolved As concentrations were significantly correlated with dissolved Fe (p<0.05) (Figure 4.3A) and dissolved Mn (p-value of 0.0086) (Figure 4.3B). The increase in arsenic concentration with iron supports the findings of the analysis of Environment Canterbury data. The significant positive relationship between dissolved As and Mn was also consistent with the findings of the Environment Canterbury data analysis. The correlations between As and Fe, and As and Mn, were also consistent with the results of a study of Waikato wells carried out by Environment Waikato (2006) but not the study of New Zealand coastal wells by Ministry of Health (2002).

Dissolved Reactive Phosphorus

Dissolved reactive phosphorus and dissolved As concentrations were significantly correlated (p<0.05) (Figure 4.3D). This positive correlation was also present in the Environment Canterbury dataset and is consistent with a study by Anawar et al (2011) which found a strong positive correlation between DRP and As in shallow wells in Bangladesh. Dissolved reactive phosphorus and As are most likely correlated due to the analogous relationship between arsenate and phosphate, which compete for the same mineral adsorption surfaces (Zeng et al., 2008). There is potential that increased fertilisation of the Canterbury Plains could result in increased As concentrations in groundwater due to ion exchange onto mineral surfaces between the phosphate and arsenate analogues.

Total, Inorganic and Organic Carbon

The correlation between dissolved As concentration and total carbon concentration was significant (p-value of 0.046) (Figure 4.3C). Total inorganic carbon and total organic carbon were not linearly correlated with dissolved As (p>0.05). However, wells with detectable As had significantly higher concentrations of total organic carbon than wells with no detectable As (p-value of 0.0044). Further, the nine wells with the highest As concentrations had significantly higher total organic carbon concentrations than the nine wells with the lowest As concentrations (p-value of 0.011). The relationship between As and total organic carbon was consistent with the findings of Ahmed et al (2004) who report that elevated organic carbon concentrations were associated with elevated As concentrations. It was also

consistent with the strong positive correlation between dissolved organic carbon and As concentration found in wells where the reductive dissolution of iron was the dominant mechanism of As release into groundwater in Bangladesh (Smedley, 2003).

Nitrate

The correlation between dissolved NO_3 and As was not statistically significant but it indicated mutual exclusion ($p<0.05$) (Figure 4.3E). A mutually exclusive relationship would be consistent with findings of previous studies by the Ministry of Health (2002) and Environment Waikato (2006). However, the observed lack of relationship between As concentration and NO_3 concentration was inconsistent with those studies which found significant negative correlations between these variables (Ministry of Health, 2002) (Environment Waikato, 2006). It was also inconsistent with overseas studies such as that by Smedley (2003).

Sulfate

Sulfate and As concentrations were significantly inversely correlated indicating a mutually exclusive relationship (Figure 4.3F). These results were consistent with the analysis of the Environment Canterbury data. The relationship between As and SO_4 was also consistent with findings of the study by Environment Waikato (2006) and studies in West Bengal and the Huhhot Basin of Inner Mongolia which found low concentrations of SO_4 in groundwaters with elevated concentrations of As (Smedley et al., 2003). The mechanism of As release into groundwater in the Huhhot Basin was believed to be the dissolution of Fe oxide minerals leading to desorption of As (Smedley et al., 2003).

Dissolved Oxygen

There was no significant correlation between dissolved As and DO concentrations ($p>0.05$). However, there was some evidence of mutual exclusion (Figure 4.3G) which is consistent with the results of the Environment Canterbury data analysis. The As concentration in wells with DO>4 mg/L was significantly higher than in wells with DO<4mg/L. The observed mutually exclusive relationship between DO and As is also consistent with a study carried

out in the Bengal Basin which found that elevated As concentrations occurred primarily in wells with an anoxic environment (Ahmed et al., 2004).

Conductivity

Dissolved As increased with groundwater conductivity (p<0.05) when four sites with high conductivities were excluded (2A, 2C, 8A and 8C) (see Figure 4.3H). The positive correlation between As and conductivity was consistent with studies by Kinniburgh et al (2003) and Anawar et al (2011) which found that wells with elevated As tended to also have elevated conductivity values, but inconsistent with the results of the analysis of Environment Canterbury data.

4.6 Coastal/Inland Analysis

A series of t-tests were carried out to determine whether there was any statistically significant difference in the As concentration of wells depending on how close they are to the coast (Table 4.6). These analyses were carried out using binary categories such as ≤1.0 km and >1.0 km from coast. There was no significant difference in As concentration based on distance from the coast (p>0.05). The results from this analysis were not consistent with the findings of the analysis of the Environment Canterbury dataset, but were consistent with a New Zealand wide study by the Ministry of Health (2002) which found no difference between As concentration in wells less than 2 km from the coast than those further inland.

Table 4.8: Statistical analysis of the As concentration in wells depending on their proximity to the coast.

Category 1	Category 2	*P*-value	Significant difference?
≤1 km from coast	>1 km from coast	0.19	No
≤1.5 km from coast	>1.5 km from coast	0.19	No
≤2 km from coast	>2 km from coast	0.22	No
≤5 km from coast	>5 km from coast	0.28	No
≤10 km from coast	>10 km from coast	0.12	No

4.7 Depth Analysis

There was no significant difference in As concentration with depth (Table 4.9). This supports the findings of the analysis of Environment Canterbury data and is consistent with some previous studies but not others, as the literature is divided on whether As concentration generally varies with depth. Other factors such as residence time and type of sediments may impact the concentration of As more than depth (Smedley et al., 2007). The results were inconsistent with a study carried out on As in New Zealand groundwater by the Ministry of Health (2002), as well as a study in Burkina Faso by Smedley et al (2007), which both found that As concentration was higher in deep wells than it was in shallow wells. In contrast, studies by Kinniburgh et al (2003) and the British Geological Survey and Department for Public Health Engineering (2001) found that shallow wells exceeded the maximum allowable values and drinking water limits more often than deep wells. The lack of relationship between As concentration and depth may indicate that As in the Canterbury groundwater is naturally occurring rather than anthropogenic. If As was originating from an anthropogenic source, at or above ground level, elevated As concentrations would be observed in shallow wells compared to deep wells.

Table 4.9: Statistical analysis of the arsenic concentration in wells depending on their depth.

Category 1	Category 2	*P*-value	Significant Difference
≤25 m	>25 m	0.24	No
≤50 m	>50 m	0.55	No
≤75 m	>75 m	0.13	No
≤100 m	>100 m	0.12	No

4.8 Seasonal Analysis

There was no significant difference in As concentration between samples collected in autumn compared to those collected mid-winter (p>0.05). Canterbury experienced a drought in 2015 when sampling was undertaken, with a rainfall of 49 mm (only 76% of the annual average rainfall) in Christchurch in July (National Institute for Water and Atmospheric Science, 2015). Additionally, Environment Canterbury (2015) reported that

81% of monitoring wells had a groundwater level less than the average for August. This drought may have masked any seasonal effects. The lack of significant seasonal variation was inconsistent with the analysis of Environment Canterbury data, but this may be due to the unusual dryness of 2015 whereas Environment Canterbury data was collected over a longer timeframe. Recharge is important in relation to As concentration. Munk et al (2011) found that As concentrations in groundwater were elevated following recharge events in Anchorage, Alaska. Seasonal differences were observed in Nepal with elevated As concentrations in summer arising as a result of aquifer recharge during the wet season (Yadav et al., 2015).

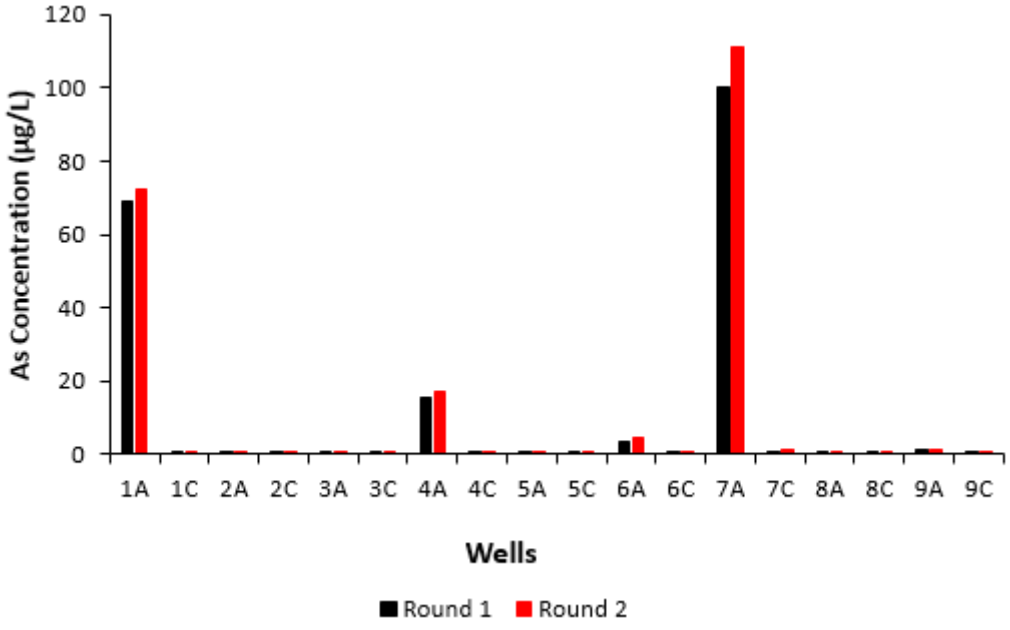


Figure 4.4: Dissolved As concentration (µg/L) in wells collected in July/winter compared to in April/autumn.

4.9 Earthquake Analysis

A paired t-test was carried out using data obtained during sampling combined with data obtained from the Environment Canterbury groundwater monitoring database. The t-test was used to determine whether the means of the As concentration in selected wells after the Canterbury earthquakes were significantly different to the means of the As concentrations in selected wells in the years following the earthquakes. There was no significant difference between the As concentrations in wells before the earthquakes and the As concentration in wells following the earthquakes (*p*-value of 0.11). This indicates that

the earthquakes did not cause a significant disturbance in As geochemistry or in the composition of groundwater.

4.10 Soil Chemistry

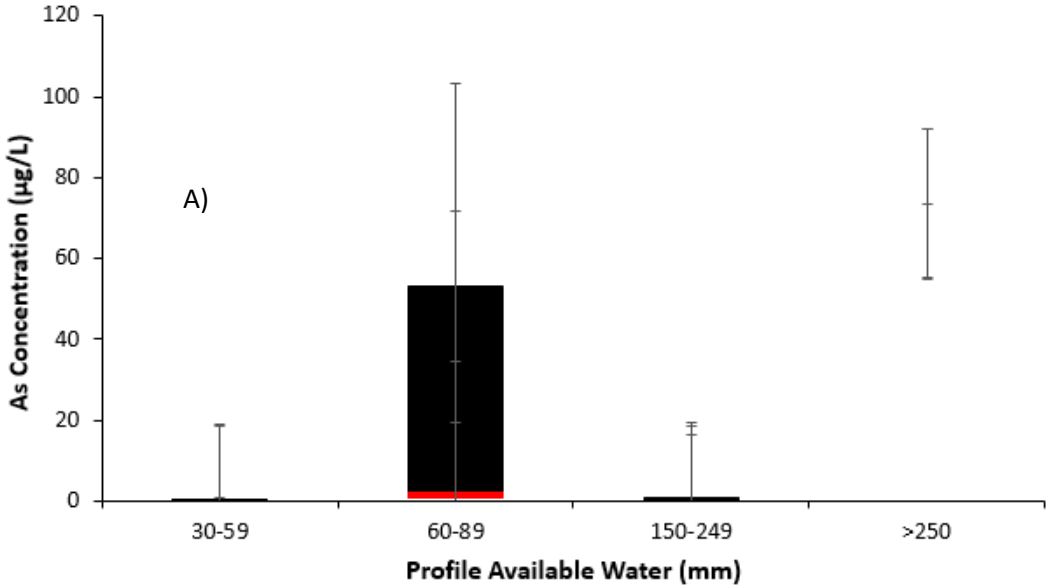
The Landcare Research soil and environmental characteristics information (presented in Appendix 2) was used to create a series of box and whisker plots that showed how sampling wells were distributed between categories. There were no relationships between As concentration and soil pH, soil drainage, flood return interval, or depth to a slowly permeable horizon, as was observed for the Environment Canterbury dataset.

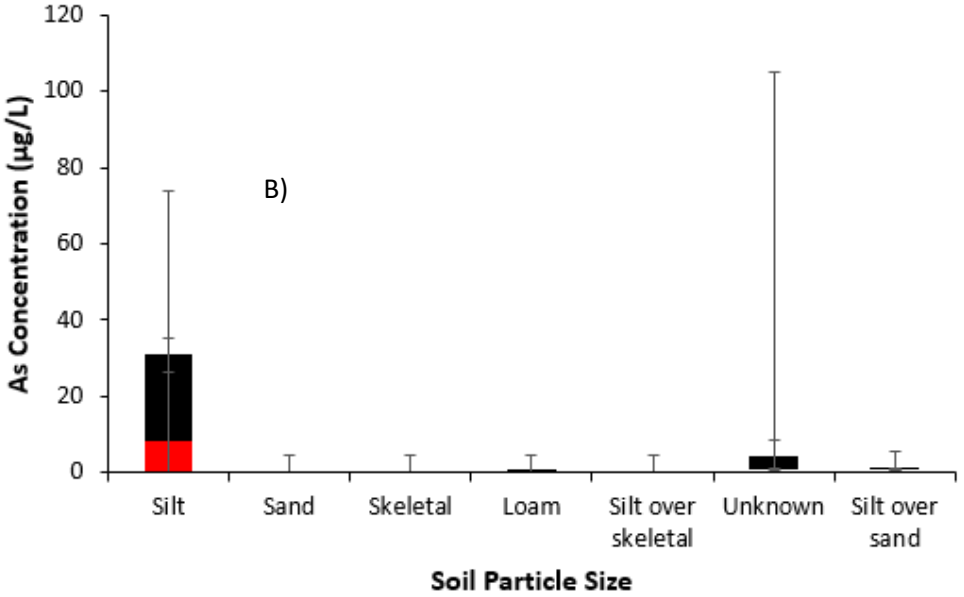
Soil Types

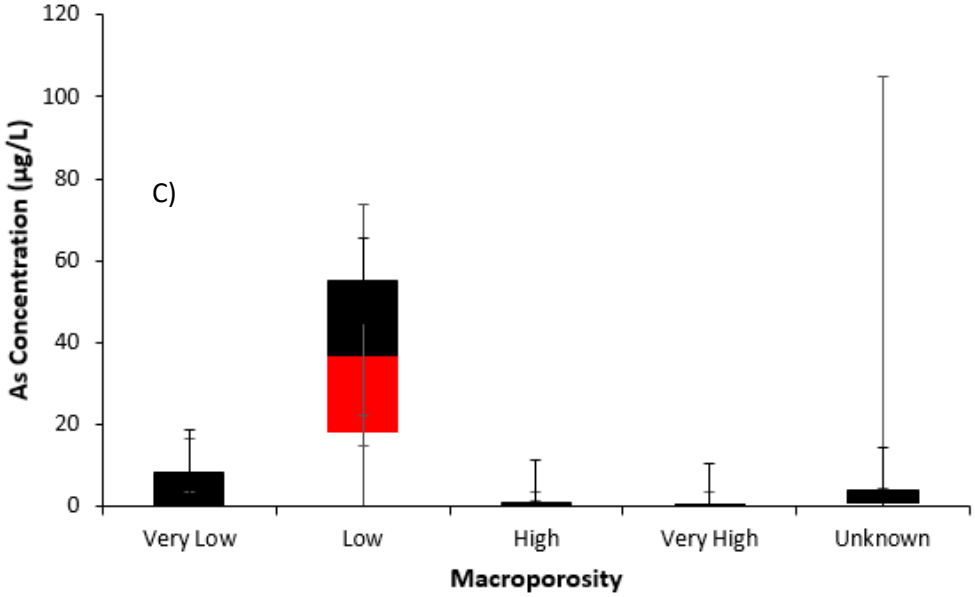
Wells with elevated As were present in orthic gley, recent gley, fragic pallic, and other unknown soils classes (Figure 4.5D). The most elevated-As well was present in fragic pallic soil, however this was the only well tested in this soil class. Wells located in both gley soil types contained groundwater with slightly elevated As. This was consistent with the analysis of Environment Canterbury data. The orthic gley category had high variation. Gley soils tend to contain water and be reducing (Landcare Research, 2016), which may be linked to the reductive dissolution mechanism of As release which can occur in strongly reducing wells.

Soil Size

All wells with elevated As were located in soils classified as silt-sized except for those in the unknown category (Figure 4.5B). This was consistent with the analysis of the Environment Canterbury data and with research by Smedley & Kinniburgh (2002) in West Bengal and Bangladesh, which found that elevated As wells were generally surrounded by silts, sands and clays. Most of the wells sampled fell within the silt category so the wells with low-As concentrations were also found in areas with silt-sized soils.







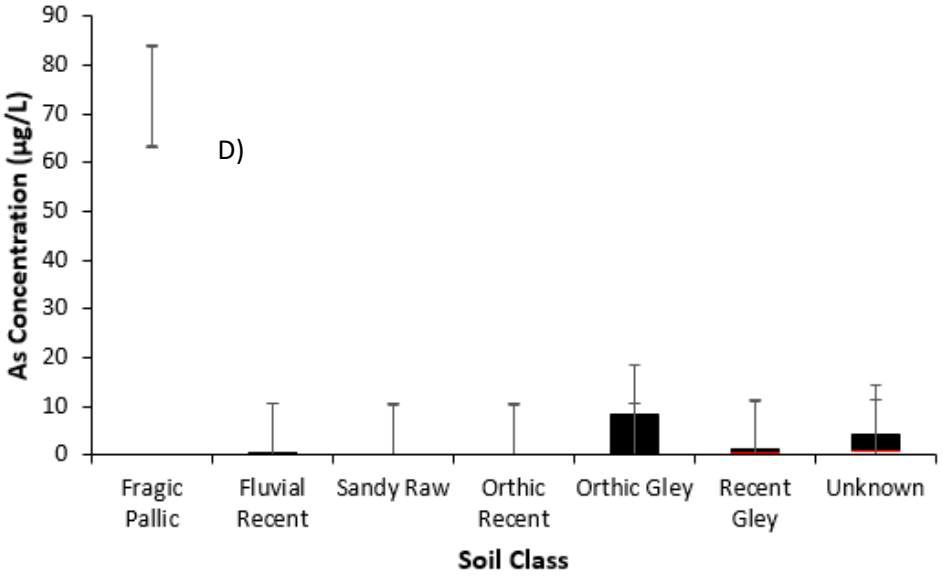


Figure 4.5 A – D: Arsenic concentration in groundwater according to soil characteristics from Landcare Research (1996) including profile available water (A), soil size (B), macroporosity (C) and soil class (D).

Macroporosity

All of the wells with elevated As concentrations were located in soils with low or very low macroporosity (except for wells in the unknown category) (Figure 4.5C) which could be due to prevailing anaerobic environment conditions and reducing environments that are conducive to the reductive dissolution of Fe and Mn oxide minerals. Low macroporosity soils may have lower DO concentrations and hence higher As concentrations.

Profile Available Water

One well with a high As concentration (70.7 µg/L) had the highest profile available water (PAW) value of >250 mm in the surrounding soils (Figure 4.5A). There was only one well in this category so it is unknown whether this pattern would hold if other wells in soils with >250 mm PAW were tested. The well with the highest As concentration (105 µg/L) in its groundwater was surrounded by soils with PAW of 60-89 mm, but there was a wide range of As concentrations in groundwater located in soils in this PAW category.

4.11 PHREEQC

To carry out PHREEQC aqueous geochemical modelling, the concentrations of As, HCO_3, Ca, Cl, Cu, Fe, K, Mg, Mn, NO_3, Na, DO, DRP, Pb, SO_4, and Zn were entered into the modelling programme along with other key physicochemical parameters such as temperature and pH. The aqueous geochemical conditions in the groundwater at each well were modelled. The results indicated that certain minerals including birnessite, bixbyite, manganite, iron hydroxide and goethite had positive saturation indices indicating that they may precipitate onto mineral surfaces and particulates in the wells. The dominant species of inorganic As in the well was As(V). Modelling indicated that nearly all wells contained common Fe and Mn oxyhydroxide minerals (Table 4.10).

The saturation index for birnessite was negative at well 5C. The saturation indices for bixbyite at wells 1C, 4C, 5A, 5C, and 9C were negative. Manganite had negative saturation indices at wells 1C, 4C, and 5C. Except for well 5A, these wells were in the ‘C’ category and

had low As concentrations. This indicates that elevated As may be less likely to occur in wells where Mn and Fe oxyhydroxide are not present in solid form. However, some wells where Mn and Fe oxyhydroxide minerals are likely to exist (based on the saturation indices) also have low As, which suggests that their presence may not be a good indicator of elevated As in groundwater. Other factors, such as DO concentration, may be a better indicator of elevated As.

Table 4.10: Saturation indices for Fe and Mn oxide and hydroxide minerals from PHREEQC modelling. '+' indicates a positive saturation index and '–' indicates a negative saturation index.

Well	Birnessite (MnO_2)	Bixbyite (Mn_2O_3)	Goethite (FeOOH)	$Fe(OH)_3$	Manganite (MnOOH)
1A	+	+	+	+	+
1C	+	–	+	+	–
2A	+	+	+	+	+
2C	+	+	+	+	+
3A	+	+	+	+	+
3C	+	+	+	+	+
4A	+	+	+	+	+
4C	+	–	+	+	–
5A	+	–	+	+	+
5C	–	–	+	+	–
6A	+	+	+	+	+
6C	+	+	+	+	+
7A	+	+	+	+	+
7C	+	+	+	+	+
8A	+	+	+	+	+
8C	+	+	+	+	+
9A	+	+	+	+	+
9C	+	–	+	+	+

4.12 Possible Mechanisms of Release

Wells with elevated As concentrations were found to generally have low DO and SO_4 concentrations, indicating reducing conditions. Significant positive relationships were confirmed between As, Fe, Mn, DRP and total organic carbon. Environment Waikato (2006)

determined that strong correlations between As, Mn and Fe were consistent with the release of sorbed As due to the reductive dissolution of Fe and Mn oxides. Based on the knowledge that wells with elevated As were reducing, with elevated Fe and Mn concentrations, my hypothesis is that the reductive dissolution of Mn- and Fe- oxides with adsorbed As species is responsible for the release of As into groundwater. The significant correlation between As and DRP indicated that elevated concentrations of DRP coincided with elevated concentrations of As. For this reason, it is considered that competitive exchange between arsenate and phosphate is also contributing to elevated As concentrations in Canterbury groundwaters.

Other mechanisms were excluded for the following reasons:

1. Canterbury is not known to have significant geothermal activity with the exception of the area along the main divide, Hanmer Springs, and a few localised areas around Christchurch (GNS Science et al., 2006).
2. There was not a positive correlation between As and SO_4 which would be observed if the oxidation of sulfide minerals was occurring.
3. There was no relationship between pH and As concentration. Additionally, there was only one pH measured that was above 8.5, which indicates that high pH values are not associated with As release in Canterbury groundwaters.

There may be a degree of saline intrusion occurring in well 8A which had a slightly elevated As concentration, significantly elevated major ion concentrations, and a high conductivity.

Chapter 5: Conclusions

5.1 Conclusions

An analysis of existing groundwater well monitoring data (from Environment Canterbury), augmented by a 12 month programme of sampling particular wells in Canterbury was undertaken. Eighteen wells were sampled twice: once in March/April and once in July. These wells were divided into two categories for the purposes of comparison: low arsenic wells and elevated arsenic wells. Several wells were found which had elevated As concentrations, some exceeding the New Zealand drinking water standard of 10 µg/L. The most contaminated wells found during sampling were located in Kaikoura, the Ohoka area, and coastal Christchurch. An examination of As monitoring data over a period of several years determined that there was no significant change in As concentration as a result of the Canterbury earthquakes in 2010 and 2011, but revealed seasonal variation. In the monitoring data, arsenic concentrations appeared to be higher in cooler/wetter months than warmer/drier months. However, this was not evident in the As concentrations from sampling, which showed no significant difference in winter samples compared to autumn samples. Given that Canterbury was experiencing a drought when samples were collected (National Institute for Water and Atmospheric Science, 2015), this may have masked seasonal effects which would usually occur.

The analysis of Environment Canterbury monitoring data did not appear to show any particular spatial trends, other than a relationship between As concentration and distance from the coast. Coastal wells (≤4.0 kilometres from coast) had elevated As concentrations compared to inland wells (>4.0 metres from coast). Again the recent sampling results did not show this relationship, but it is likely there were too few wells to see a significant relationship.

Significant linear correlations were found between As concentration and Fe, Mn, and DRP concentrations in both the monitoring data and recent sampling. Arsenic concentration was also significantly inversely related to DO and SO_4 concentrations. These correlations all

support the premise that higher As concentrations occur in anoxic groundwater in Canterbury. Elevated-As wells were found to also have elevated organic carbon concentrations, which is consistent with As-release under reducing conditions formed by the degradation of organic matter. A relationship was evident between arsenic and organic carbon concentration, so anoxic conditions may be due to organic carbon-rich horizons within the alluvial gravel hosting the aquifer.

There was little evidence for arsenic release or enrichment mechanisms such as the oxidation of As-bearing sulfide minerals, and the high pH-related release of As often observed in arid areas. The former mechanism would lead to a positive correlation between DO and As concentrations (not seen), and the latter to a positive relationship between pH and As concentration (also not seen).

The positive correlation with DRP may indicate that arsenate and phosphate are undergoing competitive adsorption on mineral surfaces. If so, the concentration of DRP in groundwater may be a contributing factor in As release into Canterbury groundwater. However, it may also simply reflect that both will be released when Fe oxides dissolves in low oxygen conditions. PHREEQC geochemical modelling showed that the groundwater in every well with As concentrations greater than 1 µg/L would have been saturated with Fe- and Mn-oxyhydroxide minerals such as birnessite, bixbyite, goethite, iron hydroxide and manganite, under oxygenated conditions. All of these minerals can adsorb arsenic and phosphate. In contrast, not all of the groundwater wells with As concentrations less than 1 µg/L would have been saturated with these minerals under the same oxygenated conditions.

In conclusion, the dominant mechanism of arsenic release into Canterbury groundwaters is hypothesised to be the reductive dissolution of the iron- and manganese oxyhydroxide minerals to which arsenic is adsorbed.

5.2 Limitations of This Study

This study was carried out over 18 months, but the sampling phase lasted for only five months and was during the significant drought experienced in 2015. The results from sampling may therefore not be representative of typical Canterbury conditions. Sampling arsenic-enriched and arsenic-depleted wells over a longer term would have helped to confirm seasonal and other variability over time, with fewer confounding factors.

Environment Canterbury's monitoring wells are not evenly distributed over Canterbury, with fewer wells located in inland Canterbury around the main divide than on the plains and along the coast. It would have been useful to include a greater number of wells from the Canterbury high country.

The study was designed so that wells with elevated As were paired with wells with low As, in order to compare the difference in well chemistry, which was a significant limitation. Sampling results showed that many wells expected to have elevated As did not, so comparing the paired wells was not an effective way to determine the factors related to, or influencing, the concentration of As in Canterbury groundwater.

5.3 Further Research

Further research into the seasonal variation of As in groundwater, based on sampling over multiple years, could determine whether there is a relationship between As concentration and other factors such as groundwater level and rainfall. It could also determine whether aquifer recharge leads to elevated As concentrations. The mechanism of As release proposed in this thesis may be corroborated by studies into the microbial transformations of As, and of As oxidation state and speciation in the groundwater. Alternatively, these studies may support an alternative mechanism of As release into groundwater.

Further studies that focus primarily on examining the relationship between As concentration and distance from the coast would help to understand the influence of

coastal proximity. Experimental studies could be carried out to determine the extent to which the application of phosphate-based fertilisers leads to displacement of arsenate from sediments into groundwater. A study of the sediments in wells with elevated As concentrations may allow the origin of this arsenic to be determined (e.g., mineralized veins in the upper Wilberforce Valley, adjacent to the Canterbury Plains, which have been shown to contain elevated arsenic (Horton et al., 2001).

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Appendices

Appendix 1: Information and Consent Sheet for Well Owners

Department Telephone: +64 3 364 2330
Email: ashlee.dolamore@pg.canterbury.ac.nz
16 March 2015

Re: A research project: The factors causing arsenic release into Canterbury groundwaters. Information Sheet for Well Owners.

My name is Ashlee Dolamore and I am a postgraduate student studying towards a Master's degree in Water Resource Management at the University of Canterbury. I will be researching and writing a thesis investigating where arsenic is present in Canterbury groundwaters and why it is there. I will sample from a selection of wells that have been tested previously and shown to have arsenic in their water, and compare this to samples from other similar wells that have not shown any arsenic contamination in the past.

Well water will be tested for a range of chemicals including arsenic, phosphate, nitrate, sulphate, calcium, chlorine, iron, manganese, zinc, organic carbon, sodium, hydrogen carbonate, potassium, bromide, magnesium, copper, chromium, and cadmium. I will also test the pH, temperature, conductivity and dissolved oxygen concentration of the water in each well. Once I have completed my primary investigation, I will use Geographical Information Systems (GIS) to map the distribution of some chemicals throughout the area of Canterbury that was sampled.

Your involvement in this project would extend to allowing me to sample from your well twice: once in March/April and once in June/July. Depending on the size of your well, sampling would take 40 - 90 minutes, once I am on-site. You do not have to be present, but can choose to be if you would like. I will send you a copy of the results for your well, when the data has been carefully checked for inclusion in my thesis.

Participation is entirely voluntary. To ensure anonymity and confidentiality, I will not include the identity of well owners in the thesis (as this is a public document), and I will assign each well a number rather than referring to a well by the owner's name. Only my supervisors and I will have access to the raw data which includes the well owners' details. The raw data will be stored on a computer that is password protected.

I am being supervised by Professor Jenny Webster-Brown and Dr Sally Gaw. Professor Webster-Brown can be contacted at jenny.webster-brown@canterbury.ac.nz and Dr Gaw can be contacted at sally.gaw@canterbury.ac.nz. They will be pleased to discuss any concerns you may have about participation in the project. This project has been reviewed and approved by the University of Canterbury Human Ethics Committee, and participants should address any complaints to The Chair, Human Ethics Committee, University of Canterbury, Private Bag 4800, Christchurch (human-ethics@canterbury.ac.nz).

If you agree to participate in the study, you are asked to complete the consent form and return to me either in person or by scanning and emailing to ashlee.dolamore@pg.canterbury.ac.nz.
Ashlee Dolamore
Department Telephone: +64 3 364 2330
Email: ashlee.dolamore@pg.canterbury.ac.nz

Factors causing arsenic release into Canterbury groundwaters

Consent Form for Well Owners.

	Initial:
I have been given a full explanation of this project and have had the opportunity to ask questions. YES/NO	
I understand what is required of me if I agree to take part in the research. YES/NO	
I understand that any information or opinions I provide will be kept confidential to the researcher and her supervisors and that any published or reported results will not identify the people or companies or groups they are affiliated with. YES/NO	
I understand that a thesis is a public document and will be available through the UC Library. YES/NO	
I understand that all raw data collected for the study will be kept in locked and secure facilities or in password protected electronic form and will be destroyed after five years. YES/NO	
I understand the risks associated with taking part and how they will be managed. YES/NO	
I understand that I am able to receive a report on the findings of the study by contacting the researcher at the conclusion of the project. YES/NO	
I understand that I can contact the researcher Ashlee Dolamore at ashlee.dolamore@pg.canterbury.ac.nz or supervisors Professor Jenny Webster-Brown and Doctor Sally Gaw at jenny.webster-brown@canterbury.ac.nz and sally.gaw@canterbury.ac.nz respectively for further information. YES/NO	
If I have any complaints, I can contact the Chair of the University of Canterbury Human Ethics Committee, Private Bag 4800, Christchurch (humanethics@canterbury.ac.nz) YES/NO	

By signing below, I agree to participate in this research project.

Name _____ Date _____

Signature _____

Please return these to me in person or scan and email to ashlee.dolamore@pg.canterbury.ac.nz before the date I have advised I will be sampling your well.
Ashlee Dolamore

Appendix 2: Soil Characteristics and Surrounding Environment

Well	Soil Drainage	Internal Soil Drainage	Soil Moisture (Profile Available Water, mm)	Depth to a Slowly Permeable Horizon (m)	Soil Permeability
1A	Poorly drained	Imperfectly drained	>250	0.9-1.35	Moderate over slow
1C	Well drained	Moderately well-drained	150-249	0.6-0.89	Moderate over slow
2A	Well drained	Well drained	150-249	>1.5	Rapid
2C	Well drained	Well drained	30-59	>1.5	Rapid
3A	Poorly drained	Poorly drained	150-249	0.0-0.44	Moderate over slow
3C	Well drained	Poorly drained	30-59	1.36-1.49	Moderate over rapid
4A	Poorly drained	Poorly drained	150-249	0.0-0.44	Moderate over slow
4C	Poorly drained	Very poorly drained	150-249	0.0-0.44	Moderate over slow
5A	Well drained	Well drained	150-249	1.39-1.49	Moderate
5C	Well drained	Well drained	150-249	1.36-1.49	Moderate
6A	Well drained	Unknown	60-89	Unknown	Unknown
6C	Well drained	Unknown	60-89	Unknown	Unknown
7A	Well drained	Unknown	60-89	Unknown	Unknown
7C	Well drained	Unknown	30-59	Unknown	Unknown
8A	Poorly drained	Poorly drained	150-249	1.36-1.49	Moderate
8C	Poorly drained	Poorly drained	150-249	1.36-1.49	Moderate
9A	Imperfectly drained	Poorly drained	150-249	1.36-1.49	Moderate
9C	Imperfectly drained	Unknown	150-249	Unknown	Unknown

Well	Macroporosity (0 – 0.6 m)	Macroporosity (0.6 – 0.9 m)	Depth to Hard Soil/ Gravel/ Rock (cm)	NZSC	Total Carbon (g C/100 g soil)	Phosphate Retention (%)
1A	Moderate	Low	>100	Fragic Pallic	2-3.9	10-29
1C	High	High	20-45	Fluvial Recent	2-3.9	10-29
2A	Very high	Very high	>100	Sandy Raw	2-3.9	10-29
2C	Very high	Very high	<20	Orthic Recent	2-3.9	30-59
3A	Low	Very low	>100	Orthic Gley	4-9.9	10-29
3C	High	Low	>100	Recent Gley	2-3.9	10-29
4A	Low	Very low	>100	Orthic Gley	4.9.9	30-59
4C	Low	Very low	>100	Orthic Gley	10-19.9	10-29
5A	High	High	>100	Fluvial Recent	2-3.9	10-29
5C	High	High	>100	Fluvial Recent	2-3.9	10-29
6A	Unknown	Unknown	>100	Unknown	Unknown	Unknown
6C	Unknown	Unknown	>100	Unknown	Unknown	Unknown
7A	Unknown	Unknown	>100	Unknown	Unknown	Unknown
7C	Unknown	Unknown	>100	Unknown	Unknown	Unknown
8A	Moderate	High	>100	Recent Gley	2-3.9	10-29
8C	Moderate	High	>100	Recent Gley	2-3.9	10-29
9A	Moderate	High	>100	Recent Gley	2-3.9	10-29
9C	Unknown	Unknown	>100	Unknown	Unknown	Unknown

Well	Topsoil Gravel Content (%)	Particle Size	Rock Outcrops and Surface Boulders	Observed Erosion Severity	Snow/ Ice Cover	Steepness Of Slope	Potential Rooting Depth (m)
1A	1-4	Silt	Non-rocky	Slight	None	Flat	1.2-1.35
1C	1-4	Silt	Non-rocky	Slight	None	Flat	0.9-1.19
2A	1-4	Sand	Non-rocky	Slight	None	Flat	1.2-1.35
2C	15-34	Skeletal	Non-rocky	Slight	None	Flat	0.25-0.44
3A	1-4	Silt	Non-rocky	Negligible	None	Flat	0.15-0.24
3C	1-4	Loam	Non-rocky	Moderate	None	Flat	0.25-0.44
4A	1-4	Silt	Non-rocky	Negligible	None	Flat	0.15-0.24
4C	1-4	Silt over skeletal	Non-rocky	Negligible	None	Flat	1.2-1.35
5A	1-4	Loam	Non-rocky	Negligible	None	Flat	1.2-1.35
5C	1-4	Loam	Unknown	Negligible	None	Flat	1.2-1.35
6A	Unknown	Unknown	Unknown	Unknown	None	Flat	Unknown
6C	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown
7A	Unknown	Unknown	Unknown	Negligible	None	Flat	Unknown
7C	Unknown	Unknown	Unknown	Negligible	None	Flat	Unknown
8A	1-4	Silt over sand	Non-rocky	Negligible	None	Flat	0.25-0.44
8C	1-4	Silt over sand	Non-rocky	Negligible	None	Flat	0.25-0.44
9A	1-4	Silt over sand	Non-rocky	Negligible	None	Flat	0.25-0.44
9C	Unknown	Unknown	Unknown	Unknown	None	Flat	Unknown

Site	Max. Salinity (g/100g soil)	Min. pH	CEC (cmoles(+)/kg)	Flood Return Interval	Soil Temperature Regime (°C)
1A	0.01-0.04	5.8-6.4	25-40	Nil	11-15 (<60 days below 5°C)
1C	0.01-0.04	5.8-6.4	25-40	Slight (<1 in 60 years)	11-15 (<60 days below 5°C)
2A	0.01-0.04	5.8-6.4	25-40	Slight (<1 in 60 years)	11-15 (<60 days below 5°C)
2C	0.01-0.04	5.5-5.7	41-70	Nil	11-15 (<60 days below 5°C)
3A	0.01-0.04	6.5-7.5	12-24	Slight (<1 in 60 years)	11-15 (<60 days below 5°C)
3C	0.15-0.29	6.5-7.5	25-40	Nil	11-15 (<60 days below 5°C)
4A	0.01-0.04	6.5-7.5	12-24	Slight (<1 in 60 years)	11-15 (<60 days below 5°C)
4C	0.01-0.04	5.8-6.4	12-24	Slight (<1 in 60 years)	11-15 (<60 days below 5°C)
5A	0.01-0.04	5.8-6.4	25-40	Slight (<1 in 60 years)	11-15 (<60 days below 5°C)
5C	0.01-0.04	5.5-5.7	25-40	Slight (<1 in 60 years)	11-15 (<60 days below 5°C)
6A	Unknown	Unknown	Unknown	Unknown	Unknown
6C	Unknown	Unknown	Unknown	Unknown	Unknown
7A	Unknown	Unknown	Unknown	Unknown	Unknown
7C	Unknown	Unknown	Unknown	Unknown	Unknown
8A	>0.7	6.5-7.5	25-40	Moderate (1 in 20 to 1 in 60 years)	11-15 (<60 days below 5°C)
8C	>0.7	6.5-7.5	25-40	Moderate (1 in 20 to 1 in 60 years)	11-15 (<60 days below 5°C)
9A	>0.7	6.5-7.5	25-40	Nil	11-15 (<60 days below 5°C)
9C	Unknown	Unknown	Unknown	Unknown	Unknown

Appendix 3: Environmental Conditions during Sampling

Round 1

	Weather			Temperature		Time of Day			Surroundings			
Site	Sun	Cloud	Rain	Cold	Warm	am	Midday	pm	Residential	Industrial	Livestock	Waterway
1A	✓	✓			✓		✓		✓		✓	✓
1C	✓	✓			✓	✓					✓	
2A		✓	✓		✓	✓					✓	
2C		✓			✓	✓			✓		✓	
3A		✓		✓		✓					✓	✓
3C		✓		✓			✓		✓			
4A	✓	✓			✓			✓	✓			
4C		✓		✓		✓					✓	
5A		✓		✓		✓			✓	✓		
5C		✓		✓		✓			✓		✓	
6A		✓	✓	✓				✓	✓			
6C	✓				✓			✓	✓			
7A	✓			✓			✓		✓			✓
7C	✓			✓		✓			✓			✓
8A	✓	✓		✓		✓			✓	✓	✓	✓
8C	✓	✓		✓			✓		✓	✓		✓
9A		✓	✓	✓			✓			✓		✓
9C		✓		✓		✓			✓			✓

Round 2

	Weather			Temperature		Time of Day			Surroundings			
Site	Sun	Cloud	Rain	Cold	Warm	am	Midday	pm	Residential	Industrial	Livestock	Waterway
1A		✓	✓	✓			✓		✓		✓	✓
1C		✓		✓		✓					✓	
2A		✓		✓		✓					✓	
2C		✓		✓		✓			✓		✓	
3A		✓	✓	✓		✓					✓	✓
3C		✓	✓	✓		✓			✓			
4A		✓	✓	✓			✓		✓			
4C		✓	✓	✓		✓					✓	
5A		✓		✓			✓		✓	✓		
5C		✓		✓				✓	✓		✓	
6A		✓		✓		✓			✓			
6C		✓		✓				✓	✓			
7A		✓		✓			✓		✓			✓
7C		✓		✓		✓			✓			✓
8A		✓		✓				✓	✓	✓	✓	✓
8C		✓		✓				✓	✓	✓		✓
9A	✓			✓		✓				✓		✓
9C	✓			✓	✓				✓			✓

Appendix 4: Additional Trace Elements

Round 1

	V (µg/L)	Cr (µg/L)	Co (µg/L)	Ni (µg/L)	Cd (µg/L)	Sb (µg/L)	Al (µg/L)
1A filtered	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<1.0
1A unfiltered	<0.1	<0.1	<0.1	0.227	<0.1	<0.4	12.7
1C filtered	0.105	<0.1	<0.1	0.140	<0.1	<0.4	1.17
1C unfiltered	0.108	<0.1	<0.1	0.132	<0.1	<0.4	1.41
2A filtered	0.583	0.146	<0.1	0.117	<0.1	<0.4	<1.0
2A unfiltered	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	2.49
2C filtered	0.417	0.121	<0.1	<0.1	<0.1	<0.4	<1.0
2C unfiltered	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	2.67
3A filtered	<0.1	<0.1	<0.1	0.644	0.472	<0.4	1.28
3A unfiltered	<0.1	<0.1	<0.1	0.441	0.191	<0.4	<1.0
3C filtered	<0.15	<0.1	<0.1	<0.1	<0.1	<0.4	<1.0
3C unfiltered	<0.1	<0.1	<0.1	0.132	<0.1	<0.4	1.32
4A filtered	<0.1	<0.1	<0.1	0.140	<0.1	<0.4	7.32
4A unfiltered	<0.1	<0.1	<0.1	0.330	<0.1	<0.4	23.2
4C filtered	0.143	<0.1	<0.1	0.188	<0.1	<0.4	1.95
4C unfiltered	0.162	<0.1	<0.1	0.150	<0.1	<0.4	2.65
5A filtered	0.130	<0.1	<0.1	0.810	0.473	<0.4	4.25
5A unfiltered	0.410	0.173	<0.1	0.185	<0.1	<0.4	1.76
5C filtered	0.185	<0.1	<0.1	0.873	<0.1	<0.4	3.5
5C unfiltered	0.177	<0.1	<0.1	0.536	<0.1	<0.4	1.15
6A filtered	0.117	<0.1	<0.1	<0.1	<0.1	<0.4	2.25
6A unfiltered	0.119	<0.1	<0.1	<0.1	<0.1	<0.4	1.58
6C filtered	1.48	1.04	<0.1	<0.1	<0.1	<0.4	1.54
6C unfiltered	1.46	0.982	<0.1	<0.1	<0.1	<0.4	1.47
7A filtered	<0.1	<0.1	0.141	0.182	<0.1	<0.4	1.13
7A unfiltered	<0.1	<0.1	0.135	0.102	<0.1	<0.4	<1.0
7C filtered	1.42	0.972	<0.1	0.935	0.397	<0.4	8.25
7C unfiltered	1.42	0.917	<0.1	<0.1	<0.1	<0.4	3.38
8A filtered	1.74	0.177	0.348	0.233	<0.1	<0.4	1.31
8A unfiltered	0.321	<0.1	<0.1	<0.1	<0.1	<0.4	1.29
8C filtered	0.456	<0.1	<0.1	0.167	<0.1	<0.4	6.15
8C unfiltered	0.825	0.198	0.183	0.268	<0.1	<0.4	130
9A filtered	6.02	0.496	<0.1	0.250	0.122	<0.4	3.24
9A unfiltered	6.07	0.480	<0.1	0.165	<0.1	<0.4	1.46
9C filtered	0.499	0.179	<0.1	0.148	<0.1	<0.4	<1.0
9C unfiltered	0.534	0.181	<0.1	0.127	<0.1	<0.4	<1.0

Please note that V is vanadium, Cr is chromium, Co is cobalt, Ni is nickel, Cd is cadmium, Sb is antimony, and Al is aluminium.

Round 2

	V	Cr	Co	Ni	Cd	Sb	Al
1A filtered	<0.1	<0.1	<0.1	0.226	<0.1	<0.4	1.42
1A unfiltered	<0.1	<0.1	<0.1	0.221	<0.1	<0.4	3.30
1C filtered	0.132	<0.1	<0.1	0.122	<0.1	<0.4	<1.0
1C unfiltered	0.132	<0.1	<0.1	0.108	<0.1	<0.4	<1.0
2A filtered	0.559	0.118	<0.1	0.245	<0.1	<0.4	2.51
2A unfiltered	0.590	0.127	<0.1	0.381	<0.1	<0.4	4.50
2C filtered	0.457	0.138	<0.1	<0.1	<0.1	<0.4	6.06
2C unfiltered	0.480	0.103	<0.1	0.169	<0.1	<0.4	<1.0
3A filtered	0.103	<0.1	<0.1	0.138	<0.1	<0.4	2.350
3A unfiltered	0.197	<0.1	<0.1	0.174	<0.1	<0.4	<1.0
3C filtered	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<1.0
3C unfiltered	<0.1	0.139	<0.1	0.287	<0.1	<0.4	1.20
4A filtered	<0.1	0.203	<0.1	0.136	<0.1	<0.4	1.03
4A unfiltered	<0.1	0.187	<0.1	0.137	<0.1	<0.4	5.83
4C filtered	0.155	<0.1	<0.1	0.148	<0.1	<0.4	<1.0
4C unfiltered	0.168	<0.1	<0.1	0.189	<0.1	<0.4	1.24
5A filtered	<0.1	<0.1	<0.1	0.180	<0.1	<0.4	<1.0
5A unfiltered	0.673	0.253	<0.1	0.108	<0.1	<0.4	1.72
5C filtered	0.210	<0.1	<0.1	1.52	<0.1	<0.4	<1.0
5C unfiltered	0.215	0.420	<0.1	1.44	<0.1	<0.4	3.86
6A filtered	<0.1	<0.1	<0.1	0.121	<0.1	<0.4	<1.0
6A unfiltered	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<1.0
6C filtered	1.65	0.909	<0.1	<0.1	<0.1	<0.4	<1.0
6C unfiltered	1.68	0.949	<0.1	<0.1	<0.1	<0.4	<1.0
7A filtered	<0.1	<0.1	0.156	0.131	<0.1	<0.4	<1.0
7A unfiltered	<0.1	0.103	0.166	0.130	<0.1	<0.4	1.70
7C filtered	1.63	0.968	<0.1	<0.1	<0.1	<0.4	1.43
7C unfiltered	1.66	1.05	<0.1	<0.1	<0.1	<0.4	3.50
8A filtered	2.03	0.298	0.391	0.278	0.114	<0.4	11.9
8A unfiltered	2.07	0.338	0.394	0.470	<0.1	<0.4	181
8C filtered	0.558	<0.1	<0.1	<0.1	<0.1	<0.4	1.44
8C unfiltered	1.13	0.145	0.210	0.252	<0.1	<0.4	19.4
9A filtered	7.79	0.585	<0.1	<0.1	<0.1	<0.4	1.36
9A unfiltered	7.58	0.569	<0.1	<0.1	<0.1	<0.4	1.10
9C filtered	0.670	0.251	<0.1	<0.1	<0.1	<0.4	<1.0
9C unfiltered	0.657	0.288	<0.1	0.107	<0.1	<0.4	2.45

Appendix 5: Analytical Duplicates

Round 1

Element	3A		5C		8A		6A EB	
	Original	Duplicate	Original	Duplicate	Original	Duplicate	Original	Duplicate
Na	5030	4960	4260	122	4340	24700	122	105
Mg	1820	1810	1430	22.2	1440	7030	22.2	19.6
Al	1.29	<1.0	3.50	3.58	1.17	<1.0	3.58	3.45
K	992	991	921	72.7	941	2290	72.7	69.6
Ca	9460	9290	12800	251	13200	5780	252	222
V	<0.1	<0.1	0.185	<0.1	0.184	0.339	<0.1	<0.1
Mn	6.37	6.33	0.152	0.534	0.159	182	0.534	0.472
Fe	96.8	99.1	20.2	3.85	18.5	25.3	3.85	3.01
Ni	0.644	0.375	0.873	0.996	0.722	<0.1	0.996	0.984
Cu	1.69	1.45	2.04	3.14	2.00	2.93	3.14	2.93
Zn	18.3	18.9	36.3	29.1	44.2	<10.0	29.1	29.3
As	<0.1	<0.1	<0.1	<0.1	<0.1	0.148	<0.1	<0.1
Cd	0.472	<0.1	<0.1	0.550	<0.1	<0.1	0.550	0.544
Pb	0.143	0.122	0.972	0.979	<0.1	<0.1	0.169	0.169

Round 2

Element	3C Sampling Duplicate		5A EB		7A		8A		9C	
	Original	Duplicate	Original	Duplicate	Original	Duplicate	Original	Duplicate	Original	Duplicate
Na	9250	9290	18.7	14.6	36700	36900	14900	14700	13100	13600
Mg	4030	4000	<10.0	<10.0	7740	7800	6370	6200	3800	4020
Al	1.40	1.01	<1.0	<1.0	<1.0	<1.0	181	194	<1.0	2.61
K	1610	1570	19.8	17.2	4160	4180	1780	1750	1420	1520
Ca	15600	15400	67.6	52.1	38000	38600	9270	9060	24900	26400
V	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.12	1.15	0.670	0.701
Cr	0.255	0.219	<0.1	<0.1	<0.1	<0.1	0.145	0.155	0.251	0.259
Mn	59.2	58.1	<0.1	<0.1	776	770	130	129	1.79	2.02
Fe	10100	10400	<1.0	<1.0	3460	3460	600	618	24.2	19.3
Co	<0.1	<0.1	<0.1	<0.1	0.156	0.164	0.210	0.226	<0.1	<0.1
Ni	0.285	0.259	<0.1	<0.1	0.131	0.148	0.252	0.273	<0.1	<0.1
Cu	<1.0	42.3	<1.0	<1.0	2.59	2.74	25.1	24.7	3.47	3.68
Zn	71.4	69.9	<10.0	<10.0	79.8	80.8	15.2	14.1	46.4	58.5
As	0.172	0.166	<0.1	<0.1	111	110	0.708	0.695	0.228	0.239
Cd	<0.1	<0.1	0.430	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	0.660	0.638	<0.1	<0.1	1.63	1.60	1.87	1.90	0.224	0.219

Please note that Na is sodium, Mg is magnesium, Al is aluminium, K is potassium, Ca is calcium, V is vanadium, Cr is chromium, Mn is manganese, Fe is iron, Co is cobalt, Ni is nickel, Cu is copper, Zn is zinc, As is arsenic, Cd is cadmium, and Pb is lead.

Appendix 6: Sampling Duplicates

	1A Duplicate	1A	2A Duplicate	2A	3A Duplicate	3A	3C Duplicate	3C
Na	28400	26100	95400	89600	6570	6410	9250	9660
Mg	9570	9170	10300	9810	2350	2340	4030	4120
Al	<1.0	1.42	<1.0	2.51	<1.0	2.35	1.40	<1.0
K	1190	1120	2390	2300	1290	1310	1610	1640
Ca	38400	38100	58700	56900	12500	12400	15700	15900
V	<0.1	<0.1	0.583	0.559	0.109	0.103	<0.1	<0.1
Cr	<0.1	<0.1	<0.1	0.118	<0.1	<0.1	0.255	<0.1
Mn	608	585	5.64	5.40	5.30	5.47	59.2	13.8
Fe	1920	1910	332	316	121	125	10500	1490
Co	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	0.239	0.226	0.404	0.245	0.150	0.138	0.285	<0.1
Cu	<1.0	1.65	<0.1	<0.1	1.45	<0.1	<0.1	<0.1
Zn	50.3	35.9	<10.0	<10.0	<10.0	<10.0	71.4	<10.0
As	76.3	72.3	0.236	0.260	0.111	0.104	0.172	0.192
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	0.446	1.23	<0.1	0.168	0.243	0.817	0.660	0.238

	4C Duplicate	4C	5A Duplicate	5A	5C Duplicate	5C	6A Duplicate	6A
Na	29300	30200	6940	7040	5010	5010	13300	13600
Mg	7630	7790	2200	2210	1645	1630	3070	3140
Al	<1.0	<1.0	1.47	<1.0	<1.0	<1.0	<1.0	<1.0
K	2020	2020	1880	1920	1070	1090	1400	1450
Ca	20800	21000	17900	18000	15000	14900	14200	14400
V	0.156	0.155	<0.1	<0.1	0.220	0.210	<0.1	<0.1
Cr	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mn	0.198	0.246	2.23	2.20	<0.1	0.169	58.1	59.1
Fe	16.2	18.5	70.2	71.6	12.8	20.6	166	166
Co	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	0.152	0.148	0.119	0.180	1.20	1.52	<0.1	0.121
Cu	2.43	1.910	13.2	27.7	3.32	4.83	<1.0	<1.0
Zn	<10.0	<10.0	<10.0	16.2	18.2	33.5	<10.0	<10.0
As	<0.1	0.102	<0.1	<0.1	0.137	0.134	4.63	4.69
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	0.528	0.806	0.493	3.01	1.63	2.39	<0.1	0.215

	6C Duplicate	6C	7C Duplicate	7C	8A Duplicate	8A	8C Duplicate	8C
Na	10000	9660	11200	10600	15000	14800	165000	159000
Mg	2520	2370	2860	2710	6410	6260	47200	45200
Al	<0.1	<0.1	1.04	1.43	12.9	11.9	4.49	1.440
K	1000	967	1050	1050	1830.0	1780	14900	14200
Ca	14200	13900	14800	13800	9260	9050	36100	34200
V	1.76	1.65	1.70	1.63	0.543	0.558	2.12	2.03
Cr	0.985	0.909	1.05	0.968	<0.1	<0.1	0.252	0.298
Mn	0.543	<0.1	2.37	2.53	121	119	1190	1140
Fe	90.7	11.9	24.8	21.4	81.5	80.3	479	173
Co	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.406	0.391
Ni	<0.1	<0.1	<0.1	<0.1	0.275	<0.1	0.222	0.278
Cu	8.47	<1.0	1.56	1.61	3.20	1.84	23.8	15.0
Zn	17.1	<10.0	<10.0	<10.0	23.8	<10.0	54.0	27.5
As	1.01	0.971	1.14	1.13	0.715	0.748	1.25	1.06
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.114
Pb	0.284	<0.1	0.679	1.11	0.699	0.887	0.260	0.605

	9A Duplicate	9A	9C Duplicate	9C
Na	25100	25600	13100	13100
Mg	5340	5540	3850	3800
Al	14.7	1.36	<0.1	<0.1
K	1770	1790	1440	1420
Ca	16100	16400	25200	24900
V	7.68	7.79	0.689	0.670
Cr	0.584	0.585	0.267	0.251
Mn	0.261	0.459	1.50	1.790
Fe	35.2	15.4	18.1	24.2
Co	<0.1	<0.1	<0.1	<0.1
Ni	<0.1	<0.1	<0.1	<0.1
Cu	<1.0	<1.0	3.57	3.47
Zn	<10.0	<10.0	33.3	46.4
As	1.39	1.42	0.231	0.228
Cd	<0.1	<0.1	<0.1	<0.1
Pb	<0.1	0.114	0.156	0.224